
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Background of the Invention]
This invention relates to the ceramic fluorescent substance blend for generally specifically changing into the white light the ultraviolet rays emitted from light emitting diode ("LED") about a white light lighting system.
[0002]
The white luminescence LED is used for the back light list of a liquid crystal display as a substitute of a small common lamp and a fluorescent lamp. S. The white luminescence LED is manufactured by forming a ceramic fluorescent substance layer in the output screen of the blue luminescence semi-conductor LED as indicated by "The Blue Laser Diode" 10.4 chapter besides Nakamura, and 216-221 pages (Springer, 1997) (the written content makes some of these descriptions by use). Conventionally, blue LED is the InGaN single quantum well mold LED, and a fluorescent substance is the cerium addition yttrium aluminum garnet ("YAG:Ce") of formula Y3aluminum5O12:Ce3+. The blue glow emitted from LED excites a fluorescent substance, and makes yellow light emit. The blue glow emitted from LED penetrates a fluorescent substance, and is mixed with the yellow light emitted from the fluorescent substance. An observer senses the color mixture light of blue glow and yellow light as the white light.
[0003]
However, the white light lighting system of a blue LED-YAG:Ce fluorescent substance has the following demerits. Conventional blue LED-YAG:Ce fluorescent substance equipment produces the white light which has the high color temperature of 6000-8000K which are equal to sunlight within the limits, and the typical color rendering characteristic (CRI) of about 70-75. If it puts in another way, the chromaticity or color coordinate of this equipment is adjoined and located in the blackbody locus between the color temperatures of 6000K and 8000K ("BBL") with the CIE chromaticity diagram shown in drawing 1 . The color temperature of this equipment can be reduced by increasing the thickness of a fluorescent substance. However, if the thickness of a fluorescent substance increases, the effectiveness of equipment will fall.
[0004]
Although a color temperature is comparatively high and the comparatively low blue LED-YAG:Ce fluorescent substance lighting system of CRI is received in the customer of an Far Eastern lighting commercial scene, generally the customer of the North America commercial scene likes a lighting system with a low color temperature, and, generally the customer of the Europe commercial scene likes the high lighting system of CRI. For example, the customer of North America likes the equipment which generally has the color temperature of 3000-4100K within the limits, and the customer of Europe likes the equipment with which CRI generally exceeds 90.
[0005]
The chromaticity coordinate and CIE chromaticity diagram which are shown in drawing 1 are explained

to some textbooks, such as "Luminescent Materials" (Springer-Verlag, 1994) 109-110 page besides KH.Butler, "Fluorescent Lamp Phosphors" (Pennsylvania State University publication office, 1980) 98-107 page, and G.Blasse, at the detail, and the written content makes some of these descriptions by use. The chromaticity coordinate (namely, color dot) located along with BBL is equation E(lambda) =Alambda-5/(e (B/T)-1) of a plank. It follows. For E, luminescence reinforcement and lambda are [the color temperature of blackbody, and A and B of luminescence wavelength and T] constants among a formula. The color coordinate located in a BBL top or its near produces the pleasant white light in an observer. CRI is relative measures which show the similarity of the color rendering properties of a lighting system, and the color rendering properties of a blackbody radiator. If the color coordinate of the trial color of the lot illuminated with the lighting system is the same as the coordinate of the same trial color irradiated by the blackbody radiator, CRI is equal to 100.
[0006]
Another demerit of blue LED-YAG:Ce fluorescent substance equipment is changing with the power with which the color output (for example, spectrum output distribution and peak emission wavelength) of LED is impressed to the band gap width of face and LED of an LED barrier layer. the time of manufacture -- the width of face of a request of actual band gap width of face -- ****** -- LED which has a barrier layer is manufactured by the fixed ratio. Therefore, the color output of this LED shifts from a desired parameter. Furthermore, even if the band gap of specific LED has desired width of face, the power impressed to LED at the time of actuation of LED has shifted plentifully from the desired value. This also becomes the cause by which the color output of LED shifts from a desired parameter. Since the light emitted from equipment contains the blue component from LED, if the color output of LED shifts from a desired parameter, the optical output from equipment will also shift from a desired parameter. When the gap from a desired parameter becomes large, the color output of equipment is visible to non-white (namely, white which blueness or yellow cut).
[0007]
furthermore, the color output of blue LED-YAG:Ce fluorescent substance equipment changes with the gaps (namely, systematic fluctuation at the time of manufacture) from the desired parameter which is alike occasionally, carries out at the time of LED lamp manufacture, and happens unescapable and daily a lot. It is because the color output of equipment is dramatically sensitive to the thickness of a fluorescent substance. If a fluorescent substance is too thin, the amount in which the light emitted from LED passes a fluorescent substance will exceed a desired amount. Then, since the output of blue LED becomes dominance, blueness cuts the optical output of LED-fluorescent substance compound equipment, and it is in sight. On the other hand, if a fluorescent substance is too thick, the blue LED light which passes a thick YAG:Ce fluorescent substance layer will become less than a desired amount. Then, since the yellow output of a YAG:Ce fluorescent substance becomes dominance, yellow cuts LED-fluorescent substance compound equipment and it appears.
[0008]
Therefore, the thickness of a fluorescent substance is an important variable which affects the color output of conventional equipment. Though regrettable, it is difficult to control thickness with an exact fluorescent substance on the occasion of the large scale production of blue LED-YAG:Ce fluorescent substance equipment. There is a case where outputting [of equipment] becomes unsuitable for a white light lighting application, plentifully as a result of the fluctuation of thickness of a fluorescent substance. That is, since the color output of equipment is visible to non-white (namely, color which blueness or yellow cut), it will fall, so that the manufacture yield of blue LED-YAG:Ce fluorescent substance equipment cannot approve.
[0009]
Moreover, blue LED-YAG:Ce fluorescent substance equipment also shows the halo effect which results from separation with blue glow and yellow light. LED has directivity and emits blue glow. However, a fluorescent substance emits yellow light isotropic (in namely, all directions). Therefore, when the optical output from equipment is seen vertically (that is, luminescence from LED is faced squarely like), light is visible to the white which blueness cut. On the other hand, when an optical output is seen from a fixed

include angle, yellow cuts light for yellow fluorescent substance luminescence to become dominance, and it is visible to it. If the optical output from this equipment is projected on a flat front face, the nimbus which yellow cut around the field which blueness cut will appear. This invention aims an above-mentioned problem at a dissolution or decreasing at least.

[0010]

[Summary of the Invention]

if this invention is caused like 1 voice -- light emitting diode and about 575- different about 495- from the 1st luminescent material which has the peak emission wavelength of about 620nm, and the 1st luminescent material -- different about 420- from the 2nd luminescent material which has the peak emission wavelength of about 550nm, and the 1st and 2nd luminescent material -- the white light lighting system containing the 3rd luminescent material which has the peak emission wavelength of about 480nm is offered.

[0011]

The white luminescence fluorescent substance blend which has the color temperature within the limits whose white lights which answer the incident radiation which has peak wavelength within the limits of 360-420nm, and are emitted from a fluorescent substance blend it is the white luminescence fluorescent substance blend which contains three or more kinds of fluorescent substances according to another mode of this invention, and are 3000-6500K, CRI exceeding 70, and the visibility exceeding 200 lm/W is offered.

[0012]

According to another mode of this invention

Radiation source,

1st APO:Eu2+ and a Mn2+ fluorescent substance (A contains one or more sorts of Sr, calcium, Ba, and Mg among a formula),

a) ASiO:Eu2+ fluorescent substance (A contains one or more sorts of Ba, calcium, Sr, and Mg among a formula),

b) an ADSiO:Eu2+ fluorescent substance (in A, D contains one or more sorts of Mg and Zn among a formula including one or more sorts of Ba, calcium, and Sr) -- and

c) AAlO:Eu2+ fluorescent substance (A contains one or more sorts of Ba, Sr, and calcium among a formula)

The 2nd fluorescent substance chosen from one or more sorts of **,

d) AMgAlO:Eu2+ fluorescent substance (A contains one or more sorts of Ba, calcium, and Sr among a formula),

e) a DPOCl:Eu2+ fluorescent substance (D contains one or more sorts of Sr, Ba, calcium, and Mg among a formula) -- and

f) EO*AlO:Eu2+ fluorescent substance (E contains one or more sorts of Ba, Sr, and calcium among a formula)

g) an EAlO:Eu2+ fluorescent substance (E contains one or more sorts of Ba, Sr, and calcium among a formula) -- and

h) GAlO:Eu2+ fluorescent substance (G contains one or more sorts of K, Li, Na, and Rb among a formula)

The 3rd fluorescent substance chosen from one or more sorts of **

A ****** white light lighting system is offered.

[0013]

The 1st fluorescent substance powder which has the peak emission wavelength of about 575 - 620nm of abbreviation according to another mode of this invention, The 2nd fluorescent substance powder which has the peak emission wavelength of about 495 - 550nm of abbreviation, The manufacture approach of a white light lighting system including the process which blends the 3rd fluorescent substance powder which has the peak emission wavelength of about 420 - 480nm of abbreviation, and prepares fluorescent substance powder mixture, and the process which adjoins light emitting diode and arranges this fluorescent substance powder mixture in a white light lighting system is offered.

[0014]
[Embodiment of the Invention]
If the trouble in the advanced technology is taken into consideration, it is desirable to obtain the white light lighting system which produces a color output with little effect by the fluctuation (for example, fluctuation of the power of LED, the band gap width of face of an LED barrier layer, and the thickness of luminescent material) in the time of actuation of equipment and a manufacture process. If this invention person etc. did not include the significant visible radiation to which the color output of radiation source-luminescent-material equipment is emitted from the radiation source (for example, LED), the color output of this equipment acquired the knowledge that the effect by this fluctuation fell. In this case, the color output of equipment does not change with the power, band gap width of face, and luminescent material of LED intentionally. The vocabulary "luminescent material" includes the fluorescent substance of the gestalt of rose powder or restoration powder preferably.
[0015]
If the white light emitted from equipment does not contain the significant visible component emitted from the radiation source (for example, LED), the color output of equipment does not change with the thickness of luminescent material intentionally. Therefore, the amount of the LED radiation which passes luminescent material (for example, fluorescent substance) does not affect the color output of equipment. This can be attained by at least two kinds of approaches.
[0016]
One of the approaches which avoids the effect to the color output of equipment is using the radiation source which emits radiation of the wavelength which is not visible to human being's eyes. For example, what is necessary is just to constitute LED so that the ultraviolet rays (UV) which have the wavelength of 380nm or less which is not visible may be emitted to human being's eyes. Furthermore, human being's eyes are not so sensitive to purple light with an ultraviolet rays of with a wavelength of 380-400nm and a wavelength of 400-420nm. When the wavelength of the radiation emitted from LED is 420nm or less, it does not ask whether the radiation emitted from LED passes a fluorescent substance, but the color output of LED-fluorescent substance equipment stops substantial therefore, influencing. This is because radiation with a wavelength of about 420nm or less does not look almost to human being's eyes.
[0017]
The 2nd approach for avoiding the effect to the color output of equipment is using a thick luminescent material which does not pass the radiation from the radiation source. For example, when LED emits the light which is 420-650nm, in order to make it the thickness of a fluorescent substance not affect the color output of equipment, the fluorescent substance should be made sufficient thickness so that the great portion of light emitted from LED may not pass a fluorescent substance. However, although it is possible, since this method of avoiding the effect of the color output on equipment reduces the power efficiency of equipment, it is not desirable.
[0018]
the above -- it depends for the color of the light to which it is emitted from equipment in any case on the class of luminescent material used chiefly. Then, in order to make it LED-fluorescent substance equipment emit the white light, the fluorescent substance should emit the white light at the time of the exposure by LED radiation.
[0019]
Furthermore, it can be made to change by using two or more kinds of fluorescent substances, so that the color parameter of a request of the color property of the white light may be suited. For example, the visibility of the color temperature of the white light and CRI, or equipment can be optimized by choosing a specific fluorescent substance by the specific ratio. For example, a fluorescent substance ratio may be chosen so that the white light lighting system which has the visibility exceeding CRI and 300 lm/W which exceed the desirable color temperature of 3000-6500K and 70 in the North America commercial scene may be obtained. Especially as an object for flashlights, the color temperature of 4000-6500K is desirable. Other fluorescent substance ratios may be chosen so that the white light

lighting system which has the visibility exceeding CRI and 200 lm/W which exceed the desirable color temperature of 3000-4100K and 90 as an exception method in the Europe commercial scene may be obtained.

[0020]

When this invention person etc. used together the 1st orange luminescence fluorescent substance which has peak emission wavelength within the limits of about 575-620nm, the 2nd bluish green color luminescence fluorescent substance which has peak emission wavelength within the limits of about 495 - 550nm of abbreviation, and the 3rd blue luminescence fluorescent substance which has about 420 - about 480 peak emission wavelength, the observer found out sensing these compound luminescence as the white light. Furthermore, in order to raise CRI of a lighting system, the 4th red luminescence fluorescent substance which has about 620 - about 670 peak emission wavelength may be added as an arbitration component.

[0021]

Drawing 2 shows the above-mentioned principle typically. In drawing 2 , the radiation 2 emitted from the radiation source 1 like LED carries out incidence to three kinds of luminescent-material layers 3 (for example, the 1st, 2nd, and 3rd above fluorescent substances). Radiation 2 may have the wavelength (for example, wavelength of 420nm or less) which human being's eyes do not sense. By the exception method, a fluorescent substance 3 may have the thickness of extent which does not make an opposite hand pass the significant radiation 2. After absorbing the radiation 2 which carried out incidence, the 1st fluorescent substance emits the orange light 4 which has peak emission wavelength within the limits of 575-620nm, the 2nd fluorescent substance emits the bluish green colored light 5 which has peak emission wavelength within the limits of 495-550nm, and the 3rd fluorescent substance emits the blue glow 6 which has peak emission wavelength within the limits of 420-480nm. When the 4th fluorescent substance exists, the red light 7 which has peak emission wavelength is emitted within the limits of 620-670nm. An observer 8 senses the combination of the orange light 4, the bluish green colored light 5, blue glow 6, and the red light 7 of an arbitration element as the white light 9. In order that drawing 2 may illustrate the concept of color mixture, the light 4, 5, 6, and 7 of a different color shows typically that it generates from a separate fluorescent substance field. However, if each fluorescent substance is mixed and the single mixed fluorescent substance layer 3 is formed, light 4, 5, 6, and 7 will come to be emitted from the same field and/or the whole fluorescent substance.

[0022]

A white light lighting system can be formed by using together a fluorescent substance and luminescent material like a scintillator with the radiation source. In addition, as for luminescent material, it is desirable to have high quantum efficiency on the specific luminescence wavelength of the radiation source. Furthermore, as for each luminescent material, it is desirable that it is transparent to the light wavelength emitted from other luminescent material.

[0023]

1. Radiation Source

The radiation source 1 should just consist of the radiation source which can make luminescence from a fluorescent substance occur. Preferably, the radiation source 1 consists of LED. However, the radiation source 1 may consist of noble gas, such as Ne in gas, such as mercury in a fluorescent lamp or a high-pressure mercury-vapor lamp, or a plasma display, Ar, and/or Xe.

[0024]

The radiation source 1 should just consist of LED to which the radiation 9 which looks white to an observer 8 from a fluorescent substance 3 is made to emit, when the radiation 2 emitted from LED carries out incidence to a fluorescent substance. For example, LED uses III-V, II-VI, or an IV-IV semi-conductor layer as a base material suitably, and is easy to consist of semiconductor diode which has the luminescence wavelength of 360-420nm. For example, LED may contain one or more semi-conductor layers which use GaN, ZnSe, or a SiC semi-conductor as a base material. Moreover, according to the request, LED may contain one or more quantum wells in the active region. Preferably, the active region of LED may include the p-n junction which consists of GaN, AlGaN, and/or an InGan semi-conductor

layer. P-n junction may be isolated by the thin non-doping InGan layer or one or more InGan quantum wells. LED may have luminescence wavelength within the limits of 370-390nm most preferably within the limits of 370-405nm within the limits of 360-420nm. However, LED with luminescence wavelength longer than 420nm may be used together with a fluorescent substance with thick thickness with which the bleedoff light from LED does not pass a fluorescent substance. For example, LED may have 370, 375, 380, 390, or wavelength like 405nm.

[0025]

In the above, the radiation source 1 of a white light lighting system has been explained as semi-conductor light emitting diode. However, the radiation source of this invention is not limited only to semi-conductor light emitting diode. For example, the radiation source may consist of laser diode or organic light emitting diode (OLED). The above-mentioned desirable white light lighting system includes the single radiation source 1. However, in order to mix the white light which improves the white light emitted or is emitted with the light of a different color, according to a request, two or more radiation sources may be used in equipment. For example, a white light lighting system may be used together with red, green, and/or blue light emitting diode within a display unit.

[0026]

2. 1st Fluorescent Substance

The 1st luminescent material should just be a fluorescent substance which emits the light which answers incident radiation 2 from the radiation source 1, and has the peak emission wavelength of about 575 - 620nm of abbreviation. When the radiation source 1 becomes within the limits which is 360-420nm from LED which has peak emission wavelength, the 1st fluorescent substance should just be a thing which has high relative visibility and quantum efficiency within the limits of 575-620nm to the incident radiation which has peak wavelength in a peak-emission-wavelength list within the limits of 360-420nm and which consists of an available fluorescent substance commercially.

[0027]

Preferably, the 1st fluorescent substance contains APO:Eu2+ and Mn2+ (A contains one or more sorts of Sr, calcium, Ba, and Mg among a formula). The 1st fluorescent substance contains most preferably pyrophosphoric-acid alkaline-earth-metal salt fluorescent substance A2P2O7:Eu2+ which doped a europium and manganese, and Mn2+. This fluorescent substance can be written to be 2(A1-x-yEuxMny) P2O7 (the inside of a formula, 0< x<=0.2, 0< y<=0.2). Preferably, A is strontium ion. Since this fluorescent substance has high visibility and high quantum efficiency to the incident radiation which has peak wavelength within the limits of 360-420nm emitted from LED, it is desirable as an object for the LED radiation sources. The 1st fluorescent substance may consist of A3P2O8:Eu2+ and Mn2+ (A contains one or more sorts of Sr, calcium, Ba, and Mg among a formula) as an exception method.

[0028]

In the pyrophosphoric-acid alkaline-earth-metal salt fluorescent substance which doped Eu2+ and Mn2+, generally Eu ion acts as a sensitizer and, generally Mn ion acts as an activator. That is, Eu ion absorbs the incidence energy (namely, photon) emitted from the radiation source, and transmits absorbed energy to Mn ion. Mn ion emits the large radiation band of width of face with the peak wavelength which changes from about 575nm to 595nm, when it is raised to an excitation state and A ion consists of Sr ion with the energy absorbed and transmitted. A shall consist of % of 50-mol Sr ion, and 50-mol % Mg ion, and you may make it become APO:Eu2+, SrMgP2O7:Eu2+ in which a Mn2+ fluorescent substance has the peak wavelength of about 615nm, and a Mn2+ fluorescent substance as an exception method.

[0029]

3. 2nd Fluorescent Substance

The 2nd luminescent material should just be a fluorescent substance which emits the light which answers incident radiation 2 from the radiation source 1, and has the peak emission wavelength of about 495 - 550nm of abbreviation. When the radiation source 1 becomes within the limits which is 360-420nm from LED which has peak emission wavelength, the 2nd fluorescent substance should just be a thing which has high relative visibility and quantum efficiency within the limits of 495-550nm to the

incident radiation which has peak wavelength in a peak-emission-wavelength list within the limits of 360-420nm and which consists of an available fluorescent substance commercially. For example, three kinds of following Eu2+ activation silicic-acid alkaline-earth-metal salts and an ulmin acid alkaline-earth-metal salt fluorescent substance suit these criteria.
[0030]
One of the fluorescent substances of these is silicic-acid alkaline-earth-metal salt fluorescent substance ASiO:Eu2+ (A contains one or more sorts of Ba, calcium, Sr, and Mg among a formula) activated by the bivalence europium. An ASiO:Eu2+ fluorescent substance has presentation A2SiO4:Eu2+, and A consists of 60% or more of Ba, 30% or less of Sr, and 10% or less of calcium preferably. When A consists of Ba or calcium, the peak emission wavelength of a fluorescent substance is about 505nm. When A consists of Sr, the peak emission wavelength of a fluorescent substance is about 580nm. Therefore, in order to obtain desired peak wavelength, A consists of Ba ion containing calcium only with little Ba ion, and/or most desirable Sr ion.
[0031]
In a silicic-acid alkaline-earth-metal salt fluorescent substance, since a europium activator permutes the grid part of alkaline earth metal, a fluorescent substance can be written to be 2(1(Ba, Sr, calcium)-xEux) SiO4 (the inside of a formula, 0< x<=0.2). The silicic-acid alkaline-earth-metal salt fluorescent substance may contain other impurities and dopants. For example, the fluorescent substance may contain the little fluorine mixed during powder processing from the fluorine content flux compound (for example, BaF2 or EuF3).
[0032]
Silicic-acid alkaline-earth-metal salt fluorescent substance ADSiO:Eu2+ (in A, D contains one or more sorts of Mg and Zn among a formula including one or more sorts of Ba, calcium, and Sr) activated by other bivalence europiums is also suitable as the 2nd fluorescent substance. Preferably, an ADSiO:Eu2+ fluorescent substance has presentation A2DSi2O7:Eu2+. The peak emission wavelength and relative quantum efficiency of each isomorphism fluorescent substance are shown in the following table I.
[0033]
[A table 1]

表 I

	A	D	A	D	A	D	A	D	A	D	A	D
	Ca	Mg	Sr	Mg	Sr	Zn	Sr/Ba	Mg	Ba	Mg	Ba	Zn
ピークλ	535		470		470		440		500		505	

[0034]
Therefore, in order to obtain desired peak wavelength, A consists of Ba ion containing calcium only with little Ba ion, or most desirable Sr ion.
[0035]
In a silicic-acid alkaline-earth-metal salt fluorescent substance, since a europium activator permutes the grid part of alkaline earth metal, a fluorescent substance can be written to be 2D (A1-xEux) SiO7 (the inside of a formula, 0< x<=0.2). The silicic-acid alkaline-earth-metal salt fluorescent substance may contain other impurities and dopants. For example, this fluorescent substance may contain the little fluorine mixed during powder processing from the fluorine content flux compound (for example, BaF2 or EuF3).
[0036]

Moreover, it is suitable for using ulmin acid alkaline-earth-metal salt fluorescent substance AAlO:Eu2+ (A containing one or more sorts of Ba, Sr, and calcium among a formula) activated by the bivalence europium as the 2nd fluorescent substance. An AAlO:Eu2+ fluorescent substance has presentation AAl2O4:Eu2+, and A consists of 50% or more of Sr, and consists of 80% or more of Sr, and 20% or less of Ba preferably. When A consists of Sr, the peak emission wavelength of a fluorescent substance is about 505nm. When A consists of Sr, the peak emission wavelength of a fluorescent substance is about 520nm. When A consists of calcium, the peak emission wavelength of a fluorescent substance is about 440nm. Therefore, in order to obtain desired peak wavelength, A consists of Sr ion or Sr, and Ba ion most preferably.

[0037]

In an ulmin acid alkaline-earth-metal salt fluorescent substance, since a europium activator permutes the grid part of alkaline earth metal, a fluorescent substance can be written to be 2(A1-xEux) aluminum 2O4 (the inside of a formula, 0< x<=0.2). The ulmin acid alkaline-earth-metal salt fluorescent substance may contain other impurities and dopants (for example, fluorine mixed from flux).

[0038]

The silicic-acid alkaline-earth-metal salt fluorescent substance activated by the europium is indicated by "Fluorescence of Eu2+Activated Silicates" 23 Philips Res.Repts[besides G.Blasse]., and 189-200 (1968) (the written content makes some of these descriptions by use) at the detail. The ulmin acid alkaline-earth-metal salt fluorescent substance activated by the europium is indicated by "Fluorescence of Eu2+Activated Alkaline-Earth Aluminates" 23 Philips Res.Repts[besides G.Blasse]., and 201-206 (1968) (the written content makes some of these descriptions by use) at the detail. Luminescence and the excitation spectrum of an above-mentioned fluorescent substance are also illustrated by these periodicals.

[0039]

In one mode of this invention, in order to optimize a color or other luminescence properties, the 2nd fluorescent substance may consist of two or more silicates and aluminate fluorescent substances according to a request. For example, the 2nd fluorescent substance is good in the combination of the combination of ASiO:Eu2+ and ADSiO:Eu2+, the combination of ASiO:Eu2+ and AAlO:Eu2+, the combination of ADSiO:Eu2+ and AAlO:Eu2+ or ASiO:Eu2+, ADSiO:Eu2+, and AAlO:Eu2+. The above-mentioned fluorescent substance can be arranged in the overlapping layers or the lighting system same as a blend.

[0040]

4. 3rd Fluorescent Substance

The 3rd luminescent material should just be a fluorescent substance which emits the light which answers incident radiation 2 from the radiation source 1, and has the peak emission wavelength of about 420 - 480nm of abbreviation. When the radiation source 1 becomes within the limits which is 360-420nm from LED which has peak emission wavelength, the 3rd fluorescent substance should just be a thing which has high visibility and quantum efficiency within the limits of 420-480nm to the incident radiation which has peak wavelength in a peak-emission-wavelength list within the limits of 360-420nm and which consists of an available fluorescent substance commercially. For example, an Eu2+ activation fluorescent substance available on two kinds of following commercial targets suits these criteria.

[0041]

An example of the 3rd fluorescent substance which has peak emission wavelength within the limits of 420-480nm is halo phosphate fluorescent substance DPOCl:Eu2+ (D contains one or more sorts of Sr, Ba, calcium, and Mg among a formula) activated by the bivalence europium. As for a DPOCl:Eu2+ fluorescent substance, it is desirable to consist of available "SECA" fluorescent substance D5 (PO4) 3Cl:Eu2+ commercially. In order to raise luminescence reinforcement, a small amount of phosphate may be permuted by a small amount of borate. The peak emission wavelength of this fluorescent substance changes according to the ratio of strontium ion and other alkaline-earth-metal ion. When D consists only of Sr ion, peak emission wavelength is 447nm. If Ba ion permutes Sr ion, peak luminescence will move to a short wavelength side, and if calcium ion permutes Sr ion, peak

luminescence will move to a long wavelength side. For example, if 0.5-mol calcium ion permutes 0.5 mols of five-mol Sr ion, peak luminescence will move to 452nm. If 0.5 mols calcium ion and 0.5-mol Ba ion permute one-mol Sr ion, peak luminescence will move to 445nm. Therefore, a desirable SECA fluorescent substance presentation is 5(Sr1-y-zBayCaz)-xEux(PO4) 3Cl (the inside of a formula, 0.01<=x<=0.2, 0<=y<=0.1, 0<=z<=0.1), and desirable peak emission wavelength is 447-450nm.
[0042]
Another example of the 3rd fluorescent substance which has peak emission wavelength within the limits of 420-480nm is ulmin acid alkaline-earth-metal salt fluorescent substance AMgAlO:Eu2+ (D contains one or more sorts of Ba, calcium, and Sr among a formula) activated by the bivalence europium. A desirable aluminate fluorescent substance has the mole ratio of various magnesium, aluminum, and oxygen, and can obtain it commercially under the name of "BAM." For example, one of the desirable BAM fluorescent substances can be written to be AMg2aluminum16O27:Eu2+ (it to be desirable that 90% or more of Ba ion is included as for the inside of a formula, and A). This fluorescent substance has presentation (Ba1-xEux) Mg2aluminum 16O27 (it is 0<=x<=0.2 among a formula, and is x= 0.07 preferably). As an exception method, BAM has mole-ratio BaMgAl10O17:Eu2+. Since an Eu2+ activator exists in the grid part of A, a BAM fluorescent substance has a luminescence peak in about 450nm. A luminescence peak moves to a long wavelength side from 450nm with the increment in the amount of barium ion permutations in strontium ion.
[0043]
Another example of the 3rd fluorescent substance which has peak emission wavelength within the limits of 420-480nm contains the bivalence europium activation aluminate fluorescent substance chosen from an EO*AlO:Eu2+ fluorescent substance, an EAlO:Eu2+ fluorescent substance, and/or a GAlO:Eu2+ fluorescent substance (E consists of one or more sorts of Ba, Sr, and calcium ion among a formula, and G contains one or more sorts of K, Li, Na, and Rb ion). Preferably, E consists of Ba ion permuted with 0 - 10% of Sr, or calcium ion, and G contains K permuted with 0 - 10% of Li, Na, or Rb ion. Preferably, an EO*AlO:Eu2+ fluorescent substance contains z(BaO) *6aluminum2O3:Eu2+ or z(Ba1-xEux) O*6aluminum 2O3 (the inside of a formula, 1<=z<=1.8, 0<=x<=0.2). As for an EAlO:Eu2+ fluorescent substance, it is desirable that BaAl12O19:Eu2+ or (Ba1-xEux) aluminum 12O19 (the inside of a formula, 0<=x<=0.2) is included. As for a GAlO:Eu2+ fluorescent substance, it is desirable that KAl11O11.07:Eu2+ or (K1-xEux) aluminum 11O11.07 (the inside of a formula, 0<=x<=0.2) is included. EO*AlO, EAlO, and a GAlO fluorescent substance The following reference : A.L.N.Stevel and A.D.M.Schrama-de Pauw, Journal of the Electrochemical Society, 123 (1976) 691, and J.M.P.J.Verstegen, Journal of the Electrochemical Society, In 121 (1974) 1623 and a list, C.R.Ronda and B.M.J.Smets, Journal of the ElectrochemicalSoci ety, It is indicated by 136 (1989) 570 and the written content makes some of these descriptions by use.
[0044]
In one mode of this invention, the 2nd fluorescent substance may consist of a blend of SECA, BAM, and/or one or more sorts of aluminate fluorescent substances according to a request in order to optimize a color or other luminescence properties.
[0045]
5. 4th Fluorescent Substance of Arbitration
The 4th luminescent material as an arbitration component should just be a fluorescent substance which emits the light which answers incident radiation 2 from the radiation source 1, and has the peak emission wavelength of about 620 - 670nm of abbreviation. A red luminescence fluorescent substance may be added to the 1st, 2nd, and 3rd fluorescent substances in order to improve CRI of the white light emitted from the combination of a fluorescent substance. Since it is the scale which shows how the trial color of CRI under the lighting from a fluorescent substance can be seen as compared with the bottom of the lighting from blackbody, if luminescence of a fluorescent substance contains each color further, the white light from a fluorescent substance will approach the white light much more from blackbody. When the radiation source 1 becomes within the limits which is 360-420nm from LED which has peak emission wavelength, the 2nd fluorescent substance should just be a thing which has high visibility and

quantum efficiency within the limits of 620-670nm to the incident radiation which has peak wavelength in a peak-emission-wavelength list within the limits of 360-420nm and which consists of an available fluorescent substance commercially. For example, the fluoro germanate fluorescent substance activated by Mn4+ suits these criteria.

[0046]

For example, a fluoro germanate fluorescent substance may contain fluoro germanium acid magnesium fluorescent substance MgO*MgF*GeO:Mn4+ (preferably commercially available 3.5 MgO(s) *0.5MgF2*GeO2:Mn4+ fluorescent substance). This fluorescent substance emits the structuring red emission band which has six peaks at a room temperature among 623-664nm.

[0047]

6. Fluorescent Substance Blend

According to one desirable mode of this invention, the 4th fluorescent substances of the 1st, the 2nd, the 3rd, and an arbitration component are scattered. Most preferably, these fluorescent substances are mixed so that a homogeneous blend may be produced. the amount of each fluorescent substance under blend -- the class of fluorescent substance -- and it is used and is dependent on the class of radiation source. However, the 4th fluorescent substance of the 1st, the 2nd, the 3rd, and an arbitration component should be blended so that the combination of the luminescence 9 from a fluorescent substance may look white to an observer 8.

[0048]

As an exception method, the 4th fluorescent substance of the 1st, the 2nd, the 3rd, and an arbitration component can also make the separate layer formed on the radiation source 1. However, the upper fluorescent substance layer should be substantially made transparence to the radiation emitted from a downward fluorescent substance.

[0049]

The presentation of a fluorescent substance powder blend can be optimized based on the peak emission wavelength of the radiation source 1 in Blend CRI and the visibility of the number of the fluorescent substances to be used, and a request, the presentation of a fluorescent substance, and a list. For example, in order to reduce the color temperature of the fluorescent substance blend to fixed excitation radiation wavelength, the ratio of blue thru/or an orange luminescence fluorescent substance may be lowered. In order to raise CRI of a fluorescent substance blend, the 4th fluorescent substance like a red luminescence fluorescent substance may be added to a blend.

[0050]

the 1st desirable voice of this invention -- the white light which the fluorescent substance blend applied like answers the incident radiation or excitation radiation which has peak wavelength within the limits of 360-420nm including three or more kinds of fluorescent substances preferably, and is emitted from a fluorescent substance blend has the color temperature of 3000-6500K within the limits, CRI exceeding 70, and the visibility exceeding 200 lm/W. Still more preferably, the visibility of a blend exceeds 264 lm/W and a color temperature is within the limits of 3300-4100K. Visibility exceeds 264 lm/W most preferably.

[0051]

The 1st, 2nd, and 3rd desirable fluorescent substances concerning the 1st desirable mode of this invention are pyrophosphoric-acid strontium, a silicic-acid alkaline-earth-metal salt, and SECA, respectively. the 1st desirable voice -- the presentation of the blend applied like -- about 55- about 75% of the weight of Sr2P2O7:Eu2+ and a Mn2+ fluorescent substance, and about 11- about 22% of the weight of a 2(Ba, Sr, calcium) SiO4:Eu2+ fluorescent substance, and about 13- about 22% of the weight of a 5 (Sr, Ba, calcium, Mg) (PO4) 3Cl:Eu2+ fluorescent substance is included.

[0052]

the 2nd desirable voice of this invention -- the white light which the fluorescent substance blend high [CRI] applied like answers the incident radiation which has peak wavelength within the limits of 360-420nm including four or more kinds of fluorescent substances preferably, and is emitted from a fluorescent substance blend has the color temperature of 3000-4100K within the limits, CRI exceeding

90, and the visibility exceeding 200 lm/W. Still more preferably, the visibility of a blend exceeds 264 lm/W and a color temperature is within the limits of 3300-3800K.
[0053]
The 1st, 2nd, 3rd, and 4th desirable fluorescent substances concerning the 2nd desirable mode of this invention are pyrophosphoric-acid strontium, a silicic-acid alkaline-earth-metal salt, SECA, and fluoro germanium acid magnesium, respectively. The presentation of the blend concerning the 2nd desirable mode Sr2P2O7:Eu2+, the Mn2+ fluorescent substance of about 11 - 43 % of the weight of abbreviation, about 9- about 15% of the weight of a 2(Ba, Sr, calcium) SiO4:Eu2+ fluorescent substance, and about 6- about 14% of the weight of a 5 (Sr, Ba, calcium, Mg) (PO4) 3Cl:Eu2+ fluorescent substance, and about 30- about 71% of the weight of a 3.5MgO*0.5MgF2*GeO2:Mn4+ fluorescent substance is included.
[0054]
However, the fluorescent substance of others which have desired peak emission wavelength instead of being the above-mentioned fluorescent substance in addition to the above-mentioned fluorescent substance may be used. For example, to the radiation sources other than LED, the fluorescent substance which has high visibility and high quantum efficiency to the incident radiation which has the peak wavelength of 254nm and 147nm can be used for a fluorescent lamp and a plasma display application, respectively. Mercury gas luminescence with a fluorescent lamp has the peak emission wavelength of 254nm, and Xe plasma discharge with a plasma display has the peak emission wavelength of 147nm.
[0055]
7. Lighting System
According to the 1st desirable operation gestalt of this invention, the 4th fluorescent substance powder of the 1st, the 2nd, the 3rd, and an arbitration component is arranged in a white light lighting system including the LED radiation source. This white light lighting system may have various structures.
[0056]
The 1st desirable structure is sketched in drawing 3 . This lighting system contains the lead wire 13 electrically attached in the light emitting diode chip 11 and the LED chip. It may consist of a thin line supported by the thick leadframe 15, and lead wire is forming the electrode of independence nature, or lead wire 13 can also exclude a leadframe. Lead wire 13 supplies a current to the LED chip 11, and makes radiation emit from the LED chip 11.
[0057]
The LED chip 11 is enclosed with the interior of shell 17, and shell 17 surrounds an LED chip and the enclosure ingredient 19. Preferably, an enclosure ingredient consists of an ultraviolet resistance epoxy resin. Shell 17 is good at glass or plastics. An enclosure ingredient is good at an epoxy resin or a polymeric material like silicone. However, the independent shell 17 is lost and you may make it the outside surface of the enclosure ingredient 19 make shell 17. The LED chip 11 can be supported by the plinth attached in the electrode of a leadframe 15 and independence nature, the pars basilaris ossis occipitalis of shell 17, shell, or a leadframe.
[0058]
The 1st desirable structure of a lighting system contains the fluorescent substance layer 21 which consists of the 4th fluorescent substance of the 1st, the 2nd, the 3rd, and an arbitration component. The fluorescent substance layer 21 can be directly formed on the upper part of the luminescence side of the LED chip 11, or a luminescence side by applying the suspension containing the 4th fluorescent substance powder of the 1st, the 2nd, the 3rd, and an arbitration component to the LED chip 11, and drying. Fluorescent substance powder forms a solid fluorescent substance layer or a solid coat 21 after desiccation. Each should make transparence shell 17 and the enclosure ingredient 19 so that the white light 23 may pass these elements. A fluorescent substance emits the white light 23 which consists of the orange light emitted, respectively from the 4th fluorescent substance of the 1st, the 2nd, the 3rd, and an arbitration component, bluish green colored light, blue glow, and red light of an arbitration component.
[0059]
Drawing 4 shows the 2nd desirable structure of the equipment concerning the 1st desirable operation gestalt of this invention. If the point of having made fluorescent substance powder scattered inside the

enclosure ingredient 19 is removed instead of forming a fluorescent substance layer on the LED chip 11, the structure of drawing 4 is the same as the thing of drawing 3 . The 1st fluorescent substance powder can also be made scattered in the single field of the enclosure ingredient 19, or can also be made scattered over the whole enclosure ingredient product. What is necessary is to add powder to a polymer precursor, to stiffen a polymer precursor subsequently, and just to solidify a polymeric material, in order to make fluorescent substance powder scattered inside an enclosure ingredient. As an exception method, fluorescent substance powder may be mixed into an epoxy resin enclosure ingredient. Other fluorescent substance powder way-that-should-be methods can also be used. After carrying out preliminary mixing of the fluorescent substance powder, powder mixture may be added into the enclosure ingredient 19, or fluorescent substance powder may be separately added into the enclosure ingredient 19. As an exception method, the solid fluorescent substance layer 21 which consists of the 4th fluorescent substance of the 1st, the 2nd, the 3rd, and an arbitration component may be inserted into the enclosure ingredient 19 according to a request. With this structure, the fluorescent substance layer 21 absorbs the radiation 25 emitted from LED, answers it, and emits the white light 23.

[0060]

Drawing 5 shows the 3rd desirable structure of the equipment concerning the 1st desirable operation gestalt of this invention. If the point in which the fluorescent substance layer 21 containing the 4th fluorescent substance of the 1st, the 2nd, the 3rd, and an arbitration component was formed on shell 17 is removed instead of forming a fluorescent substance layer on the LED chip 11, the structure of drawing 5 is the same as the thing of drawing 3 . Although forming in the inner surface of shell 17 is desirable as for the fluorescent substance layer 21, the fluorescent substance layer 21 may be formed in the outside surface of shell according to a request. The fluorescent substance layer 21 may be formed in all the front faces of shell, or may be formed only in the crowning of the front face of shell 17.

[0061]

Of course, the operation gestalt of drawing 3 -5 may be combined and a fluorescent substance may be arranged in any two places, all three places, or other locations, for example, it may dissociate from shell, and you may arrange, or may also include in LED.

[0062]

According to the 2nd desirable operation gestalt of this invention, the 4th powder of the 1st, the 2nd, the 3rd, and an arbitration component is arranged in a white light lighting system including the fluorescent lamp radiation source. Some fluorescent lamps are sketched in drawing 6 . A lamp 31 contains the fluorescent substance coat 35 which consists of the 4th fluorescent substance of the 1st, the 2nd, the 3rd, and an arbitration component on the front face (preferably inner surface) of a lamp cover 33. moreover, the fluorescent lamp 31 -- a lamp -- it is desirable to include a mouthpiece 37 and cathode 39. The lamp cover 33 has held the gas (for example, mercury) which answers the electrical potential difference impressed to cathode 39, and emits ultraviolet rays.

[0063]

According to the 3rd desirable operation gestalt of this invention, the 4th fluorescent substance powder of the 1st, the 2nd, the 3rd, and an arbitration component is arranged in the white light lighting system containing plasma display equipment. S. The volume Shionoya and on W.M.Yen, AC like the equipment indicated by "Phosphor Handbook" (1987 CRC Pres, 1999)623-639 page (the written content makes some of these descriptions by use), or DC plasma display panel can use all plasma display equipments. Drawing 7 sketches one cel of DC plasma display equipment 41. A cel includes the noble gas space 48 in the fluorescent substance layer 46 which consists of the 4th fluorescent substance of the anode plate 45 with 44 or 1 or more cathode of the 1st glass plate 42 and 43 or 1 or more glass plates [2nd], the 1st, the 2nd, the 3rd, and an arbitration component, and barrier rib 47 list. With AC plasma display equipment, an additional dielectric layer is prepared between cathode and the gas space 48. When an electrical potential difference is impressed between an anode plate 45 and cathode 44, the noble gas in space 48 emits the vacuum ultraviolet radiation (VUV) of short wavelength, the fluorescent substance layer 46 is excited and the white light is made to emit.

[0064]

8. Processing Approach
Each fluorescent substance may be manufactured, for example by what kind of ceramic powder method (for example, a wet chemistry method or a solid phase technique).
[0065]
The manufacture approach of the 1st fluorescent substance which consists of a pyrophosphoric-acid strontium fluorescent substance which doped a europium and manganese preferably includes the following processes. First, the raw material compound of the 1st fluorescent substance is manually blended mixed within a crucible, or it blends or mixes mechanically within another, suitable container (for example, ball mill), and raw material powder mixture is prepared. A raw material compound may consist of what kind of oxide, phosphate, a hydroxide, an oxalate, a carbonate, and/or a nitrate system fluorescent substance raw material compound. As a desirable fluorescent substance raw material compound, phosphoric-acid hydrogen strontium (SrHPO4), manganese carbonate (MnCO3), europium oxide (Eu 2O3), and phosphoric-acid hydrogen ammonium (NH4) (HPO4) powder are mentioned. (NH4) HPO4 powder is preferably added with 2% excessive amount of a stoichiometric ratio per [to generate] one mol of 1st fluorescent substance. Moreover, according to a request, Sr compound of an excessive amount may be added a little. Moreover, when calcium, barium, and/or magnesium are wanted to permute some or all of strontium, calcium, barium, and a magnesium raw material compound may be added. Next, raw material powder mixture is heated for about 1 to 5 hours in about 300-800 degrees C (preferably 600 degrees C) air. Next, the obtained powder is blended again, subsequently it calcinates in about 1000-1250 degrees C (preferably 1000 degrees C) reducing atmosphere, and a baking fluorescent substance lump or a cake is obtained. Baking of the raw material ambient atmosphere mixture is preferably carried out for 4 to 10 hours (preferably 8 hours) in the furnace of the ambient atmosphere which consists of nitrogen and 0.1 - 10% of hydrogen, subsequently a furnace is turned off, and it cools in the same ambient atmosphere.
[0066]
Preferably, the manufacture approach of the 2nd desirable (Ba, Sr, calcium) 2SiO4:Eu2+ fluorescent substance includes the following processes. First, the raw material compound of a fluorescent substance is manually blended mixed within a crucible, or it blends or mixes mechanically within another, suitable container (for example, ball mill), and raw material powder mixture is prepared. A raw material compound may consist of what kind of oxide, a hydroxide, an oxalate, a carbonate, and/or a nitrate system fluorescent substance raw material compound. As a desirable fluorescent substance raw material compound, a barium carbonate (BaCO3), a strontium carbonate (SrCO3), a calcium carbonate (CaCO3), europium oxide (Eu 2O3), and a silicic acid (SiO2*xH2O) are mentioned. Preferably, flux of the amount of 0.5-3 mol %, such as CaF2, is added per one mol of generation fluorescent substances. Next, raw material powder mixture is first calcinated for 5 to 7 hours in a 1200-1400-degree C carbon content ambient atmosphere (for example, charcoal content ambient atmosphere), and the 1st baking fluorescent substance lump or cake is obtained. Subsequently, the obtained cake is ground and ground and it considers as powder. This powder is annealed or calcinated in about 900-1200-degree C reducing atmosphere next, and the 2nd baking fluorescent substance lump or cake is obtained. Preferably, powder is annealed for 2 to 6 hours in the furnace of the ambient atmosphere which consists of nitrogen and 0.1 - 10% of hydrogen.
[0067]
A solid baking fluorescent substance lump is ground to the 1st fluorescent substance powder, and fluorescent substance powder may enable it to apply him to some white light lighting systems easily. What is necessary is just to use crushing, grinding, or the pulverizing method (for example, wet grinding, dry type grinding, jet milling, or crushing) suitably, in order to use a solid fluorescent substance lump as the 1st fluorescent substance powder. A solid lump is preferably given to propanol, a methanol, and/or underwater wet grinding, and it dries.
[0068]
The 3rd and 4th fluorescent substances are commercially available as fluorescent substance powder, and the exact manufacture approach is not important. The synthesis method of BAM and a SECA

fluorescent substance is indicated by editing besides S.Shionoya, "Phosphor Handbook" (1987 CRC Press, 1999)398-399 page, and 416-419 pages, and the written content makes some of these descriptions by use. Generally, by the manufacture approach of a commercial BAM fluorescent substance, the start raw material which consists of flux (for example, aluminum fluoride or barium chloride) of a barium carbonate, a magnesium carbonate, an alumina or an aluminum hydroxide, europium oxide, and an arbitration component is blended. Next, raw material powder mixture is calcinated in about 1200-1400-degree C reducing atmosphere, and a baking fluorescent substance lump or a cake is obtained. Under the same conditions, choke crushing of the cake may be carried out and it may be re-calcinated. By the manufacture approach of a commercial SECA fluorescent substance, the start raw material which consists of a strontium carbonate, orthophosphoric acid strontium, a strontium chloride, and europium oxide is blended. Next, raw material powder mixture is calcinated in about 1000-1200-degree C reducing atmosphere, and a baking fluorescent substance lump or a cake is obtained. Subsequently, grinding of a cake obtains fluorescent substance powder.

[0069]

Next, the 4th fluorescent substance powder of the 1st, the 2nd, the 3rd, and an arbitration component is blended or mixed, and a fluorescent substance powder blend or mixture is prepared. Powder may be manually blended within a crucible and may be mechanically blended with another, suitable container (for example, ball mill). It cannot be overemphasized that the fluorescent substance powder blend may contain five or more kinds of powder according to a request. A lump may be pulverized and blended as an exception method.

[0070]

Next, a fluorescent substance powder blend is arranged in a white light lighting system. For example, a fluorescent substance powder blend may be arranged on an LED chip, it may be made scattered in an enclosure ingredient, or you may apply on the surface of shell as mentioned above about the 1st desirable operation gestalt of this invention.

[0071]

In applying a fluorescent substance powder blend to an LED chip or shell, it carries out the coat of an LED chip or the shell front face using the suspension which consists of a fluorescent substance powder blend and a liquid. Suspension may contain the binder which dissolved into the solvent as an arbitration component. Preferably, a binder consists of an organic substance (for example, a nitrocellulose or ethyl cellulose) which dissolved into the solvent (for example, butyl acetate or a xylol). A binder heightens the adhesion force of a powder particle to the adhesion force and LED, or shell of powder particles. However, according to a request, in order to simplify processing, a binder may be excluded. What is necessary is to dry and heat suspension and just to evaporate a binder after spreading. A fluorescent substance powder blend acts as a fluorescent substance layer 21 after solvent desiccation.

[0072]

What is necessary is to add a fluorescent substance blend to a polymer precursor, to stiffen a polymer precursor subsequently, and just to solidify a polymeric material, in making fluorescent substance blends scattered in the enclosure ingredient 19. As an exception method, a fluorescent substance blend may be mixed into an epoxy resin enclosure ingredient. The other fluorescent substance scattered methods may be used.

[0073]

What is necessary is just to carry out the coat of the inner surface of a lamp or a plasma display using the suspension which consists of a fluorescent substance powder blend and a liquid, in arranging a fluorescent substance blend in a fluorescent lamp or a plasma display. Suspension may contain the binder which dissolved into the solvent as an arbitration component as above-mentioned.

[0074]

9. Example

It does not pass over the following examples to instantiation, and they do not limit the technical range of this invention.

[0075]

Example 1
Three sorts of blends which consist of three kinds of fluorescent substances were prepared by the above-mentioned approach. The presentation of a blend was changed according to the peak emission wavelength of the radiation source used with each blend. Generally, about the LED radiation source which has peak emission wavelength or excitation wavelength within the limits of 370-405nm, the amount of the 1st orange luminescence fluorescent substance under blend was increased, so that excitation wavelength was long, and the amount of the 2nd bluish green color luminescence fluorescent substance and the 3rd blue luminescence fluorescent substance was reduced. The CIE color coordinate (ccx and ccy), the color temperature, CRI, and the visibility of a blend are collectively shown in the following table II at excitation wavelength, the presentation of a blend, and a list.
[0076]
[A table 2]

表 II

励起 λ	蛍光体ブレンド (WT %)	ccx	ccy	色温度 (K)	CRI	視感度 (lm/W)
380 mm	SrP (57.5) BASI (21.5) SECA (21.0)	.4011	.3807	3507	70.5	346.4
390 mm	SrP (61.4) BASI (19.4) SECA (19.2)	.3995	.3830	3565	70.7	347.3
405 mm	SrP (73.7) BASI (12.1) SECA (14.2)	.3899	.3791	3767	72.3	349.6

[0077]
The following abbreviations were used in the above-mentioned table. BASI=(Ba 0.65, Sr 0.2, calcium 0.1, Eu0.05)2SiO4, SECA=(Sr, Ba, calcium) 5 (PO4) 3Cl:Eu2+, SrP=Sr2P2O7:Eu2+, Mn2+. Visibility is defined as a product of the luminous intensity of equipment, and 683 lm/W. Here, 683 lm/W is 555nm in peak luminous intensity. The luminous intensity of equipment is defined as (integralF(lambda) Y (lambda) dlambda)/(integralF(lambda) dlambda) (F (lambda) is an emission spectrum among a formula, and Y (lambda) is the sensitivity curve of an eye). The color temperature of a blend changed from 3507K to 3767K, CRI changed from 70.5 to 72.3, and visibility changed from 346.4 lm/W to 349.6 lm/W as illustrated by Table II. These high visibility blends are desirable as an object for white light lighting systems sold in the lighting commercial scene of North America.
[0078]
Example 2
Three sorts of blends which consist of four kinds of fluorescent substances were prepared by the above-mentioned approach. The presentation of a blend was changed according to the peak emission wavelength of the radiation source used with each blend. Generally, about the LED radiation source which has peak emission wavelength or excitation wavelength within the limits of 370-405nm, the amount of the 1st, 2nd, and 3rd fluorescent substances under blend was increased, so that excitation wavelength was long, and the amount of the 4th fluorescent substance was reduced. The CIE color coordinate (ccx and ccy), the color temperature, CRI, and the visibility of a blend are collectively shown in the following table III at excitation wavelength, the presentation of a blend, and a list.
[0079]
[A table 3]

表 III

励起 λ	蛍光体ブレンド (WT %)	ccx	ccy	色温度 (K)	CRI	視感度 (lm/W)
380 mm	SrP (12.7) BASI (10.0) SECA (7.4) MgF (69.9)	.4017	.3835	3519	93	285
390 mm	SrP (17.6) BASI (11.8) SECA (9.0) MgF (61.6)	.4065	.3793	3374	93.5	272.2
405 mm	SrP (41.5) BASI (14.2) SECA (12.8) MgF (31.5)	.3967	.3743	3557	91.3	264.7

[0080]
The following abbreviations were used in the above-mentioned table. BASI=(Ba 0.65, Sr 0.2, calcium 0.1, Eu0.05)2SiO4, SECA=(Sr, Ba, calcium) 5 (PO4) 3Cl:Eu2+, SrP=Sr2P2O7:Eu2+, Mn2+, and MgF=3.5MgO*0.5MgF2*GeO2:Mn4+. The color temperature of a blend changed from 3374K to 3557K, CRI changed from 91.3 to 93.5, and visibility changed from 264.7 lm/W to 285 lm/W as illustrated by Table III. It is clear from Table III that addition of the 4th red luminescence fluorescent substance brings about remarkable buildup of CRI. These high CRI blends are desirable as an object for white light lighting systems sold in the lighting commercial scene in Europe.
[0081]
In the above, the desirable operation gestalt has been explained for the purpose of instantiation. However, probably the above explanation does not limit the technical range of this invention, and the summary of this invention and various modification in technical within the limits, application, and a permutation will be obvious to this contractor.
[Brief Description of the Drawings]
[Drawing 1]
It is the graph which shows a CIE chromaticity diagram.
[Drawing 2]
It is the schematic drawing of the white light lighting system concerning 1 operation gestalt of this invention.
[Drawing 3]
It is the outline sectional view of the lighting system using LED concerning the 1st desirable operation gestalt of this invention.
[Drawing 4]
It is the outline sectional view of the lighting system using LED concerning the 1st desirable operation gestalt of this invention.
[Drawing 5]
It is the outline sectional view of the lighting system using LED concerning the 1st desirable operation gestalt of this invention.
[Drawing 6]
It is the outline sectional view of the lighting system using the fluorescent lamp concerning the 2nd

desirable operation gestalt of this invention.
[Drawing 7]
It is the outline sectional view of the lighting system using the plasma display concerning the 3rd desirable operation gestalt of this invention.
[Description of Notations]
1 Radiation Source
2 Radiation
3 Fluorescent Substance
4 Orange Light
5 Bluish Green Colored Light
6 Blue Glow
7 Red Light
8 Observer
9 White Light
11 Light Emitting Diode Chip
13 Lead Wire
15 Leadframe
17 Shell
19 Enclosure Ingredient
21 Luminescent Material
23 White Light
25 Radiation
31 Fluorescent Lamp
33 Lamp Cover
35 Fluorescent Substance Coat
37 Lamp -- Mouthpiece
39 Cathode
41 Traffic Signal
42 1st Glass Plate
43 2nd Glass Plate
44 Cathode
45 Anode Plate
46 Fluorescent Substance Layer
47 Barrier Rib
48 Noble Gas Space

[Translation done.]

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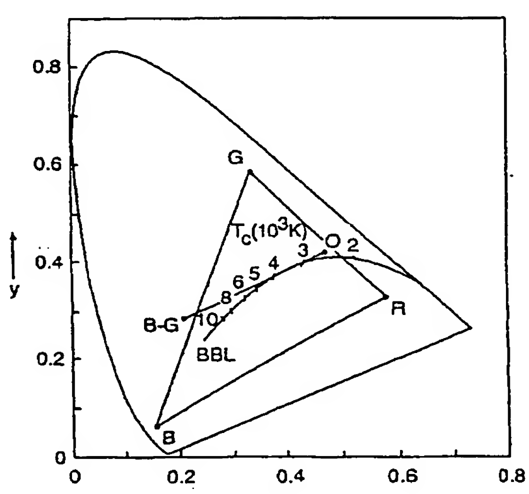
最終頁に続く

(54)【発明の名称】ＬＥＤ素子用の白色発光蛍光体ブレンド

(57)【要約】
発光ダイオード（１１）と、２以上のピーク発光波長を有する１種類以上の発光材料（２１）とを含む青緑色照明装置であって、２以上のピーク発光波長の発光ＣＩＥ色座標がＣＩＥ色度図で五辺形の領域内に位置し、五辺形の頂点が下記のＣＩＥ色座標を有する青緑色照明装置が提供される。e）ｘ＝０．０１３７及びｙ＝０．４８３１、b）ｘ＝０．２２４０及びｙ＝０．３８９０、c）ｘ＝０．２８００及びｙ＝０．４５００、g）ｘ＝０．２８７９及びｙ＝０．５１９６、並びにh）ｘ＝０．０１０８及びｙ＝０．７２２０。かかる照明装置（５１）は、交通信号機（４１）の緑色灯として使用することができる。発光材料は、$(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$（「BAM」）及び$(Ba_{1-x}Eu_x)Mg_{2-y}Mn_yAl_{16}O_{27}$（「BAMMn」）蛍光体（式中、０＜ｘ≦０．２、０＜ｙ≦０．５）のブレンドでよい。
【選択図】図１



【特許請求の範囲】
【請求項１】
発光ダイオード（１１）と、２以上のピーク発光波長を有する１種以上の発光材料（２１）とを含む青緑色照明装置であって、前記２以上のピーク発光波長の発光ＣＩＥ色座標がＣＩＥ色度図で五辺形の領域内に位置し、前記五辺形の頂点が下記のＣＩＥ色座標を有する青緑色照明装置。
ｅ）ｘ＝０．０１３７及びｙ＝０．４８３１、
ｂ）ｘ＝０．２２４０及びｙ＝０．３８９０、
ｃ）ｘ＝０．２８００及びｙ＝０．４５００、
ｇ）ｘ＝０．２８７９及びｙ＝０．５１９６、並びに
ｈ）ｘ＝０．０１０８及びｙ＝０．７２２０。
【請求項２】
前記装置から放出される光は前記発光ダイオード（１１）から放出される有意の可視成分を含まない、請求項１記載の装置。
【請求項３】
前記発光ダイオード（１１）のピーク発光波長が３６０～４２０ｎｍの範囲内にある、請求項２記載の装置。
【請求項４】
前記発光ダイオード（１１）が３７０～４０５ｎｍの範囲内にピーク発光波長を有するＩｎＧａＮ活性層を含む、請求項３記載の装置。
【請求項５】
前記発光材料（２１）の発光ＣＩＥ色座標がｘ＝０．１±０．０５及びｙ＝０．５２±０．０５である、請求項４記載の装置。
【請求項６】
前記１種以上の発光材料の発光ＣＩＥ色座標がＣＩＥ色度図で四辺形の領域内に位置し、前記四辺形の頂点が下記のＣＩＥ色座標を有する、請求項１記載の装置。
ａ）ｘ＝０．０００及びｙ＝０．５０６、
ｂ）ｘ＝０．２２４及びｙ＝０．３８９、
ｃ）ｘ＝０．２８０及びｙ＝０．４５０、並びに
ｄ）ｘ＝０．０００及びｙ＝０．７３０。
【請求項７】
前記１種以上の発光材料の発光ＣＩＥ色座標がＣＩＥ色度図で四辺形の領域内に位置し、前記四辺形の頂点が下記のＣＩＥ色座標を有する、請求項１記載の装置。
ｅ）ｘ＝０．０１３７及びｙ＝０．４８３１、
ｆ）ｘ＝０．２０９４及びｙ＝０．３９５３、
ｇ）ｘ＝０．２８７９及びｙ＝０．５１９６、並びに
ｈ）ｘ＝０．０１０８及びｙ＝０．７２２０。
【請求項８】
前記１種以上の発光材料（２１）が単一の$AMgAlO:Eu^{2+},Mn^{2+}$蛍光体を含み、ＡがＢａ、Ｃａ及びＳｒの１種以上を含む、請求項１記載の装置。
【請求項９】
前記$AMgAlO:Eu^{2+},Mn^{2+}$蛍光体が$AMg_2Al_{16}O_{27}:Eu^{2+},Mn^{2+}$蛍光体を含み、Ａが９０％以上のＢａを含む、請求項８記載の装置。
【請求項１０】
前記$AMg_2Al_{16}O_{27}:Eu^{2+},Mn^{2+}$蛍光体が$Ba_{1-x}Eu_xMg_{2-y}Mn_yAl_{16}O_{27}$蛍光体を含み、$0<x\leqq 0.2$であり、$0.05\leqq y\leqq 0.5$である、請求項９記載の装置。
【請求項１１】
前記１種以上の発光材料（２１）が
ｉ）$EO*AlO:Eu^{2+},Mn^{2+}$蛍光体（式中、ＥはＢａ、Ｓｒ及びＣａの１種以

上を含む）、
ii）$EAlO:Eu^{2+}, Mn^{2+}$蛍光体（式中、EはBa、Sr及びCaの1種以上を含む）、及び
iii）$GAlO:Eu^{2+}, Mn^{2+}$蛍光体（式中、GはK、Li、Na及びRbの1種以上を含む）
から選択される単一の蛍光体を含む、請求項1記載の装置。

【請求項12】
前記$EO*AlO:Eu^{2+}, Mn^{2+}$蛍光体が$xBaO*6Al_2O_3:Eu^{2+}, Mn^{2+}$を含み、前記$EAlO:Eu^{2+}, Mn^{2+}$蛍光体が$(Ba_{1-x}Eu_x)Al_{12-y}Mn_yO_{19-0.5y}$を含み、前記$GAlO:Eu^{2+}, Mn^{2+}$蛍光体が$(K_{1-x}Eu_x)Al_{11-y}Mn_yO_{11.07-0.5y}$を含む、請求項11記載の装置。

【請求項13】
前記1種以上の発光材料（21）が、505nmより短い第1のピーク発光波長を有する第1の蛍光体及び505nmより長い第2のピーク発光波長を有する第2の蛍光体を含む、請求項1記載の装置。

【請求項14】
前記第1のピーク発光波長が440～455nmの範囲内にあり、前記第2のピーク発光波長が510～525nmの範囲内にある、請求項13記載の装置。

【請求項15】
前記第1の蛍光体が材料（21）が
a）$AMgAlO:Eu^{2+}$蛍光体（式中、AはBa、Ca及びSrの1種以上を含む）、
b）$DPOCl:Eu^{2+}$蛍光体（式中、DはSr、Ba、Ca及びMgの1種以上を含む）、
c）$EO*AlO:Eu^{2+}$蛍光体（式中、EはBa、Sr及びCaの1種以上を含む）、
d）$EAlO:Eu^{2+}$蛍光体（式中、EはBa、Sr及びCaの1種以上を含む）、及び
e）$GAlO:Eu^{2+}$蛍光体（式中、GはK、Li、Na及びRbの1種以上を含む）
の1種以上を含む、請求項14記載の装置。

【請求項16】
前記第2の蛍光体が材料（21）が
f）$AMgAlO:Eu^{2+}, Mn^{2+}$蛍光体（式中、AはBa、Ca及びSrの1種以上を含む）、
g）$EO*AlO:Eu^{2+}, Mn^{2+}$蛍光体（式中、EはBa、Sr及びCaの1種以上を含む）、
h）$EAlO:Eu^{2+}, Mn^{2+}$蛍光体（式中、EはBa、Sr及びCaの1種以上を含む）、及び
i）$GAlO:Eu^{2+}, Mn^{2+}$蛍光体（式中、GはK、Li、Na及びRbの1種以上を含む）
の1種以上を含む、請求項15記載の装置。

【請求項17】
前記$AMgAlO:Eu^{2+}$蛍光体が$AMg_2Al_{16}O_{27}:Eu^{2+}$（式中、Aは90%以上のBaを含む）を含み、前記$DPOCl:Eu^{2+}$蛍光体が$(Sr, Ba, Ca, Mg)_5(PO_4)_3Cl:Eu^{2+}$を含み、前記$AMgAlO:Eu^{2+}, Mn^{2+}$蛍光体が$AMg_2Al_{16}O_{27}:Eu^{2+}, Mn^{2+}$（式中、Aは90%以上のBaを含む）を含み、前記$EO*AlO:Eu^{2+}$蛍光体が$xBaO*6Al_2O_3:Eu^{2+}$を含み、前記$EAlO:Eu^{2+}$蛍光体が$(Ba_{1-x}Eu_x)Al_{12}O_{19}$を含み、前記$GAlO:Eu^{2+}$蛍光体が$(K_{1-x}Eu_x)Al_{11}O_{11.07}$を含み、前記

$EO*AlO:Eu^{2+},Mn^{2+}$蛍光体が$xBaO*6Al_2O_3:Eu^{2+},Mn^{2+}$を含み、前記$EAlO:Eu^{2+},Mn^{2+}$蛍光体が$(Ba_{1-x}Eu_x)Al_{12-y}Mn_yO_{19-0.5y}$を含み、前記$GAlO:Eu^{2+},Mn^{2+}$蛍光体が$(K_{1-x}Eu_x)Al_{11-y}Mn_yO_{11.07-0.5y}$を含む、請求項１５記載の装置。

【請求項１８】
前記$AMg_2Al_{16}O_{27}:Eu^{2+}$蛍光体が$(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$（式中、$0<x\leqq0.2$）を含み、前記$(Sr,Ba,Ca,Mg)_5(PO_4)_3Cl:Eu^{2+}$蛍光体が$(Sr_{1-y-z}Ba_yCa_z)_{5-x}Eu_x(PO_4)_3Cl$（式中、$0.01\leqq x\leqq0.2$、$0\leqq y\leqq0.1$、$0\leqq z\leqq0.1$）を含み、前記$AMg_2Al_{16}O_{27}:Eu^{2+}$蛍光体が$(Ba_{1-x}Eu_x)Mg_{2-y}Mn_yAl_{16}O_{27}$（式中、$0<x\leqq0.2$、$0<y\leqq0.5$）を含み、前記$xBaO*6Al_2O_3:Eu^{2+}$蛍光体が$Ba_{0.73}Eu_{0.07}Mn_{0.20}Al_{10.9}O_{17.2}$を含み、前記$(Ba_{1-x}Eu_x)Al_{12-y}Mn_yO_{19-0.5y}$蛍光体が$(Ba_{0.86}Eu_{0.14})Al_{11.60}Mn_{0.40}O_{18.80}$を含み、前記$(K_{1-x}Eu_x)Al_{11-y}Mn_yO_{11.07-0.5y}$蛍光体が$(K_{0.86}Eu_{0.14})Al_{10.80}Mn_{0.20}O_{10.97}$を含む、請求項１７記載の装置。

【請求項１９】
前記第１の蛍光体が$(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$（式中、$0<x\leqq0.2$）を含み、前記第２の蛍光体が$(Ba_{1-x}Eu_x)Mg_{2-y}Mn_yAl_{16}O_{27}$（式中、$0<x\leqq0.2$、$0<y\leqq0.5$）を含む、請求項１８記載の装置。

【請求項２０】
前記１種以上の発光材料（２１）が、前記第１の蛍光体及び前記第２の蛍光体を約３０：７０～約８：９２の重量比で含む、請求項１９記載の装置。

【請求項２１】
前記第１の蛍光体と前記第２の蛍光体との重量比が約１８：８２である、請求項２０記載の装置。

【請求項２２】
前記第１の蛍光体及び前記第２の蛍光体が散在しているか、或いは前記第１の蛍光体及び前記第２の蛍光体が別個の重なり合った層をなす、請求項２１記載の装置。

【請求項２３】
前記第１の蛍光体及び前記第２の蛍光体の少なくとも一方が２種以上の蛍光体のブレンドを含む、請求項１３記載の装置。

【請求項２４】
前記発光ダイオード（１１）を収容したシェル（１７）と、
前記シェル（１７）と前記発光ダイオード（１１）との間に配置された封入材料（１９）とをさらに含んでいて、前記１種以上の発光材料が１種以上の蛍光体を含むと共に、
ａ）前記蛍光体が前記発光ダイオード（１１）の表面に塗布されているか、
ｂ）前記蛍光体が前記封入材料（１９）中に散在しているか、或いは
ｃ）前記蛍光体が前記シェル（１７）に塗布されている、請求項１記載の装置。

【請求項２５】
前記青緑色照明装置（５１）を収容する交通信号機ハウジング（４３）と、前記青緑色照明装置（５１）の前方に配置された交通信号灯レンズ（４５）とをさらに含む、請求項２４記載の装置。

【請求項２６】
Eu^{2+}活性化剤から放出された放射が第１のピーク発光波長を生じ、Mn^{2+}活性化剤から放出された放射が第２のピーク発光波長を生じる、請求項１記載の装置。

【請求項２７】
ハウジング（４３）と、
１以上のレンズ（４５）と、
４２０ｎｍ以下のピーク発光波長を有する放射源（１）と、

２以上のピーク発光波長を有する１種以上の発光材料（３）とを含む交通信号機であって、前記２以上のピーク発光波長の発光ＣＩＥ色座標がＣＩＥ色度図で四辺形の領域内に位置し、前記四辺形の頂点が下記のＣＩＥ色座標を有する、交通信号機。
ａ）ｘ＝０．０００及びｙ＝０．５０６、
ｂ）ｘ＝０．２２４及びｙ＝０．３８９、
ｃ）ｘ＝０．２８０及びｙ＝０．４５０、並びに
ｄ）ｘ＝０．０００及びｙ＝０．７３０。

【請求項２８】
前記放射源（１）が発光ダイオード（１１）を含む、請求項２７記載の交通信号機。

【請求項２９】
前記２以上のピーク発光波長の発光ＣＩＥ色座標がｘ＝０．１±０．０５及びｙ＝０．５２±０．０５である、請求項２８記載の交通信号機。

【請求項３０】
前記１種以上の発光材料（１）が、$(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$蛍光体（式中、０＜ｘ≦０．２）と$(Ba_{1-x}Eu_x)Mg_{2-y}Mn_yAl_{16}O_{27}$蛍光体（式中、０＜ｘ≦０．２、０＜ｙ≦０．５）とを約３０：７０～約８：９２の重量比で混合したブレンドを含む、請求項２９記載の交通信号機。

【請求項３１】
前記重量比が約１８：８２である、請求項３０記載の交通信号機。

【請求項３２】
第１のピーク発光波長を有する第１の蛍光体粉末と第２のピーク発光波長を有する第２の蛍光体粉末とを混合して、ＣＩＥ色度図で五辺形の領域内に位置する発光ＣＩＥ色座標を有し、前記五辺形の頂点が下記のＣＩＥ色座標を有するような蛍光体粉末混合物を調製する工程と、
前記蛍光体粉末混合物（３、２１）を放射源（１）に隣接して青緑色照明装置内に配置する工程とを含む青緑色照明装置の製造方法。
ｅ）ｘ＝０．０１３７及びｙ＝０．４８３１、
ｂ）ｘ＝０．２２４０及びｙ＝０．３８９０、
ｃ）ｘ＝０．２８００及びｙ＝０．４５００、
ｇ）ｘ＝０．２８７９及びｙ＝０．５１９６、並びに
ｈ）ｘ＝０．０１０８及びｙ＝０．７２２０。

【請求項３３】
前記放射源（１）が発光ダイオード（１１）を含む、請求項３２記載の方法。

【請求項３４】
前記発光ダイオード（１１）のピーク発光波長が３７０～４０５ｎｍの範囲内にあり、前記蛍光体粉末混合物（２１）の発光ＣＩＥ色座標がｘ＝０．１±０．０５及びｙ＝０．５２±０．０５である、請求項３３記載の方法。

【請求項３５】
前記混合工程が、
ａ）ＡＭｇＡｌＯ：Eu^{2+}蛍光体（式中、ＡはＢａ、Ｃａ及びＳｒの１種以上を含む）、及び
ｂ）ＤＰＯＣｌ：Eu^{2+}蛍光体（式中、ＤはＳｒ、Ｂａ、Ｃａ及びＭｇの１種以上を含む）
の１種以上から選択される第１の蛍光体粉末と、
ｃ）ＡＭｇＡｌＯ：Eu^{2+}，Mn^{2+}蛍光体（式中、ＡはＢａ、Ｃａ及びＳｒの１種以上を含む）、
ｄ）ＥａＯ＊ＡｌＯ：Eu^{2+}，Mn^{2+}蛍光体（式中、ＥはＢａ、Ｓｒ及びＣａの１種以上を含む）、
ｅ）ＥＡｌＯ：Eu^{2+}，Mn^{2+}蛍光体（式中、ＥはＢａ、Ｓｒ及びＣａの１種以上を含む）、及び

f）ＧＡｌＯ：Eu^{2+}，Mn^{2+}蛍光体（式中、ＧはＫ、Ｌｉ、Ｎａ及びＲｂの１種以上を含む）
の１種以上から選択される第２の蛍光体粉末とを混合することを含む、請求項３４記載の方法。
【請求項３６】
前記第１の蛍光体粉末と前記第２の蛍光体粉末とを混合する前記工程が、$(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$（式中、０＜ｘ≦０．２）と$(Ba_{1-x}Eu_x)Mg_{2-y}Mn_yAl_{16}O_{27}$（式中、０＜ｘ≦０．２、０＜ｙ≦０．５）とを約３０：７０～約８：９２の重量比で混合することを含む、請求項３５記載の方法。
【請求項３７】
前記重量比が約１８：８２である、請求項３６記載の方法。
【請求項３８】
前記発光ダイオード（１１）をシェル（１７）内に配置する工程と、前記シェル（１７）に封入材料（１９）を充填する工程とをさらに含む、請求項３３記載の方法。
【請求項３９】
ａ）前記蛍光体粉末混合物と溶媒とを含む懸濁液を前記発光ダイオード（１１）の表面に塗布し、前記懸濁液を乾燥させる工程、
ｂ）前記封入材料（１９）中に前記蛍光体粉末混合物（２１）を散在させる工程、或いは
ｃ）前記蛍光体粉末混合物と溶媒とを含む懸濁液を前記シェル（１７）に塗布し、前記懸濁液を乾燥させる工程
をさらに含む、請求項３８記載の方法。
【請求項４０】
前記蛍光体粉末混合物（２１）の発光ＣＩＥ色座標がＣＩＥ色度図で四辺形の領域内に位置し、前記四辺形の頂点が下記のＣＩＥ色座標を有する、請求項３２記載の方法。
ａ）ｘ＝０．０００及びｙ＝０．５０６、
ｂ）ｘ＝０．２２４及びｙ＝０．３８９、
ｃ）ｘ＝０．２８０及びｙ＝０．４５０、並びに
ｄ）ｘ＝０．０００及びｙ＝０．７３０。
【請求項４１】
前記照明装置（５１）を交通信号機ハウジング（４３）内に配置する工程をさらに含む、請求項４０記載の方法。
【請求項４２】
前記蛍光体粉末混合物の発光ＣＩＥ色座標がＣＩＥ色度図で四辺形の領域内に位置し、前記四辺形の頂点が下記のＣＩＥ色座標を有する、請求項３２記載の方法。
ｅ）ｘ＝０．０１３７及びｙ＝０．４８３１、
ｆ）ｘ＝０．２０９４及びｙ＝０．３９５３、
ｇ）ｘ＝０．２８７９及びｙ＝０．５１９６、並びに
ｈ）ｘ＝０．０１０８及びｙ＝０．７２２０。
【請求項４３】
前記照明装置を自動車用ディスプレイ内に配置する工程をさらに含む、請求項４２記載の方法。
【発明の詳細な説明】
【０００１】
【発明の背景】
本発明は一般に白色光照明装置に関し、具体的には、発光ダイオード（「ＬＥＤ」）から放出された紫外線を白色光に変換するためのセラミック蛍光体ブレンドに関する。
【０００２】
白色発光ＬＥＤは、液晶ディスプレイのバックライト並びに小型の常用ランプ及び蛍光ランプの代替品として使用されている。Ｓ．Ｎａｋａｍｕｒａ他，“Ｔｈｅ Ｂｌｕｅ Ｌａｓｅｒ Ｄｉｏｄｅ”１０．４章，２１６～２２１頁（Ｓｐｒｉｎｇｅｒ社、１９９７

）（その記載内容は援用によって本明細書の一部をなす）に記載されているように、白色発光ＬＥＤは青色発光半導体ＬＥＤの出力面にセラミック蛍光体層を形成することによって製造される。従来、青色ＬＥＤはＩｎＧａＮ単一量子井戸型ＬＥＤであり、蛍光体は式$Y_3Al_5O_{12}:Ce^{3+}$のセリウム添加イットリウムアルミニウムガーネット（「ＹＡＧ：Ｃｅ」）である。ＬＥＤから放出された青色光は蛍光体を励起して黄色光を放出させる。ＬＥＤから放出された青色光は蛍光体を透過し、蛍光体から放出された黄色光と混合される。観察者は青色光と黄色光との混色光を白色光として感知する。

【０００３】
しかし、青色ＬＥＤ－ＹＡＧ：Ｃｅ蛍光体の白色光照明装置は以下の短所を有する。従来の青色ＬＥＤ－ＹＡＧ：Ｃｅ蛍光体装置は、太陽光に匹敵する６０００～８０００Ｋの範囲内の高い色温度及び約７０～７５の典型的な演色指数（ＣＲＩ）を有する白色光を生ずる。換言すれば、この装置の色度又は色座標は図１に示すＣＩＥ色度図で６０００Ｋ及び８０００Ｋの色温度の間の黒体軌跡（「ＢＢＬ」）に隣接して位置する。この装置の色温度は、蛍光体の厚さを増大させることで低下させることができる。しかし、蛍光体の厚さが増すと装置の効率が低下してしまう。

【０００４】
色温度が比較的高くＣＲＩの比較的低い青色ＬＥＤ－ＹＡＧ：Ｃｅ蛍光体照明装置は極東の照明市場の顧客には受入れられるが、北米市場の顧客は一般に色温度の低い照明装置を好み、ヨーロッパ市場の顧客は一般にＣＲＩの高い照明装置を好む。例えば、北米の顧客は一般に３０００～４１００Ｋの範囲内の色温度を有する装置を好み、ヨーロッパの顧客は一般にＣＲＩが９０を上回る装置を好む。

【０００５】
図１に示す色度座標及びＣＩＥ色度図は、Ｋ．Ｈ．Ｂｕｔｌｅｒ，“Ｆｌｕｏｒｅｓｃｅｎｔ　Ｌａｍｐ　Ｐｈｏｓｐｈｏｒｓ”（ペンシルヴェニア州立大学出版局、１９８０）９８～１０７頁、及びＧ．Ｂｌａｓｓｅ他，“Ｌｕｍｉｎｅｓｃｅｎｔ　Ｍａｔｅｒｉａｌｓ”（Ｓｐｒｉｎｇｅｒ－Ｖｅｒｌａｇ社、１９９４）１０９～１１０頁など幾つかの教科書に詳細に説明されており、その記載内容は援用によって本明細書の一部をなす。ＢＢＬに沿って位置する色度座標（すなわち、色点）は、プランクの方程式$E(\lambda)=A\lambda^{-5}/(e^{(B/T)}-1)$に従う。式中、Ｅは発光強度、λは発光波長、Ｔは黒体の色温度、Ａ及びＢは定数である。ＢＢＬ上又はその近傍に位置する色座標は、観察者に快い白色光を生ずる。ＣＲＩは、照明装置の演色性と黒体放射体の演色性との類似度を示す相対的測度である。照明装置で照明された一組の試験色の色座標が黒体放射体で照射された同じ試験色の座標と同じであれば、ＣＲＩは１００に等しい。

【０００６】
青色ＬＥＤ－ＹＡＧ：Ｃｅ蛍光体装置のもう一つの短所は、ＬＥＤの色出力（例えば、スペクトル出力分布及びピーク発光波長）がＬＥＤ活性層のバンドギャップ幅及びＬＥＤに印加される電力と共に変化することである。製造時、実際のバンドギャップ幅が所望の幅と大小異なる活性層を有するＬＥＤが一定の比率で製造される。従って、かかるＬＥＤの色出力は所望のパラメーターからずれる。さらに、特定のＬＥＤのバンドギャップが所望の幅を有していても、ＬＥＤの動作時にＬＥＤに印加される電力は所望の値からはずれることが多々ある。これもＬＥＤの色出力が所望のパラメーターからずれる原因となる。装置から放出される光はＬＥＤからの青色成分を含むので、ＬＥＤの色出力が所望のパラメーターからずれると、装置からの光出力も所望のパラメーターからずれる。所望のパラメーターからのずれが大きくなると、装置の色出力は非白色（すなわち、青味又は黄味がかった白色）に見える。

【０００７】
さらに、青色ＬＥＤ－ＹＡＧ：Ｃｅ蛍光体装置の色出力は、ＬＥＤランプ製造時に往々にして不可避的かつ日常的に起こる所望のパラメーターからのずれ（すなわち、製造時の系統的変動）により大きく変化する。装置の色出力が蛍光体の厚さに非常に敏感だからである。蛍光体が薄すぎると、ＬＥＤから放出される光が蛍光体を通過する量は所望の量を超

える。すると、青色ＬＥＤの出力が優勢になるため、ＬＥＤ－蛍光体複合装置の光出力は青味がかって見える。他方、蛍光体が厚すぎると、厚いＹＡＧ：Ｃｅ蛍光体層を通過する青色ＬＥＤ光が所望の量よりも少なくなる。そこでＹＡＧ：Ｃｅ蛍光体の黄色出力が優勢になるため、ＬＥＤ－蛍光体複合装置は黄味がかって見える。

【０００８】

従って、蛍光体の厚さは従来の装置の色出力に影響を及ぼす重要な変数である。残念ながら、青色ＬＥＤ－ＹＡＧ：Ｃｅ蛍光体装置の大規模生産に際して蛍光体の正確な厚さを制御することは困難である。蛍光体の厚さが変動する結果、装置の出力が白色光照明用途には不適当となる場合が多々ある。つまり、装置の色出力が非白色（すなわち、青味又は黄味がかった色）に見えるため、青色ＬＥＤ－ＹＡＧ：Ｃｅ蛍光体装置の製造歩留りが許容し得ないほど低下してしまう。

【０００９】

また、青色ＬＥＤ－ＹＡＧ：Ｃｅ蛍光体装置は、青色光と黄色光との分離に原因するハロー効果も示す。ＬＥＤは、方向性をもって青色光を放出する。しかし、蛍光体は黄色光を等方的に（すなわち、すべての方向に）放出する。従って、装置からの光出力を垂直に（すなわち、ＬＥＤからの発光を直視するように）見ると、光は青味がかった白色に見える。他方、光出力を一定の角度から見ると、黄色蛍光体発光が優勢になるに光は黄味がかって見える。かかる装置からの光出力を平坦な表面に投射すると、青味がかった領域の周囲に黄味がかった光輪が現われる。本発明は、上述の問題を解消もしくは少なくとも低減することを目的とする。

【００１０】

【発明の概要】

本発明の一態様によれば、発光ダイオードと、約５７５～約６２０ｎｍのピーク発光波長を有する第１の発光材料と、第１の発光材料とは異なる約４９５～約５５０ｎｍのピーク発光波長を有する第２の発光材料と、第１及び第２の発光材料とは異なる約４２０～約４８０ｎｍのピーク発光波長を有する第３の発光材料とを含む白色光照明装置が提供される。

【００１１】

本発明の別の態様によれば、３種類以上の蛍光体を含む白色発光蛍光体ブレンドであって、３６０～４２０ｎｍの範囲内にピーク波長を有する入射放射に応答して蛍光体ブレンドから放出される白色光が３０００～６５００Ｋの範囲内の色温度、７０を上回るＣＲＩ、及び２００１ｍ／Ｗを上回る視感度を有する白色発光蛍光体ブレンドが提供される。

【００１２】

本発明の別の態様によれば、

放射源と、

第１のＡＰＯ：Eu^{2+}，Mn^{2+}蛍光体（式中、ＡはＳｒ、Ｃａ、Ｂａ及びＭｇの１種以上を含む）と、

ａ）ＡＳｉＯ：Eu^{2+}蛍光体（式中、ＡはＢａ、Ｃａ、Ｓｒ及びＭｇの１種以上を含む）、

ｂ）ＡＤＳｉＯ：Eu^{2+}蛍光体（式中、ＡはＢａ、Ｃａ及びＳｒの１種以上を含み、ＤはＭｇ及びＺｎの１種以上を含む）、及び

ｃ）ＡＡｌＯ：Eu^{2+}蛍光体（式中、ＡはＢａ、Ｓｒ及びＣａの１種以上を含む）

の１種以上から選択される第２の蛍光体と、

ｄ）ＡＭｇＡｌＯ：Eu^{2+}蛍光体（式中、ＡはＢａ、Ｃａ及びＳｒの１種以上を含む）、

ｅ）ＤＰＯＣｌ：Eu^{2+}蛍光体（式中、ＤはＳｒ、Ｂａ、Ｃａ及びＭｇの１種以上を含む）、及び

ｆ）ＥＯ＊ＡｌＯ：Eu^{2+}蛍光体（式中、ＥはＢａ、Ｓｒ及びＣａの１種以上を含む）

ｇ）ＥＡｌＯ：Eu^{2+}蛍光体（式中、ＥはＢａ、Ｓｒ及びＣａの１種以上を含む）、及び

ｈ）ＧＡｌＯ：Eu^{2+}蛍光体（式中、ＧはＫ、Ｌｉ、Ｎａ及びＲｂの１種以上を含む）の１種以上から選択される第３の蛍光体と
を含む白色光照明装置が提供される。
【００１３】
本発明の別の態様によれば、約５７５～約６２０ｎｍのピーク発光波長を有する第１の蛍光体粉末と、約４９５～約５５０ｎｍのピーク発光波長を有する第２の蛍光体粉末と、約４２０～約４８０ｎｍのピーク発光波長を有する第３の蛍光体粉末とをブレンドして蛍光体粉末混合物を調製する工程と、該蛍光体粉末混合物を発光ダイオードに隣接して白色光照明装置内に配置する工程とを含む白色光照明装置の製造方法が提供される。
【００１４】
【発明の実施の形態】
先行技術での問題点を考慮すれば、装置の動作時及び製造プロセスにおける変動（例えば、ＬＥＤの電力、ＬＥＤ活性層のバンドギャップ幅、及び発光材料の厚さの変動）による影響の少ない色出力を生じる白色光照明装置を得ることが望ましい。本発明者等は、放射源－発光材料装置の色出力が放射源（例えば、ＬＥＤ）から放出される有意の可視放射を含まなければ、かかる装置の色出力はかかる変動による影響が低下するという知見を得た。この場合、装置の色出力はＬＥＤの電力、バンドギャップ幅及び発光材料によって有意には変化しない。「発光材料」という用語は、好ましくはばら粉末又は充填粉末の形態の蛍光体を包含する。
【００１５】
装置から放出される白色光が放射源（例えば、ＬＥＤ）から放出される有意の可視成分を含まなければ、装置の色出力は発光材料の厚さによって有意には変化しない。従って、発光材料（例えば、蛍光体）を通過するＬＥＤ放射の量は装置の色出力に影響を及ぼさない。これは、少なくとも２通りの方法で達成できる。
【００１６】
装置の色出力に対する影響を回避する方法の一つは、人間の目には見えない波長の放射を放出する放射源を使用することである。例えば、人間の目には見えない３８０ｎｍ以下の波長を有する紫外線（ＵＶ）を放出するようにＬＥＤを構成すればよい。さらに、人間の目は波長３８０～４００ｎｍの紫外線及び波長４００～４２０ｎｍの紫色光にはさほど敏感でない。従って、ＬＥＤから放出される放射の波長が４２０ｎｍ以下のときは、ＬＥＤから放出される放射が蛍光体を通過するか否かを問わず、ＬＥＤ－蛍光体装置の色出力は実質的な影響を受けなくなる。これは、波長約４２０ｎｍ以下の放射は人間の目にはほとんど見えないためである。
【００１７】
装置の色出力に対する影響を回避するための第２の方法は、放射源からの放射を通過させない厚い発光材料を使用することである。例えば、ＬＥＤが４２０～６５０ｎｍの可視光を放出する場合に、蛍光体の厚さが装置の色出力に影響を及ぼさないようにするには、ＬＥＤから放出される可視光の大半が蛍光体を通過しないように蛍光体を十分な厚さにすべきである。ただし、装置の色出力への影響を回避するこの方法は可能ではあるが、装置の出力効率を低下させるので好ましくない。
【００１８】
上記いずれの場合も、装置から放出される可視光の色は専ら使用する発光材料の種類に依存する。そこで、ＬＥＤ－蛍光体装置が白色光を放出するようにするには、蛍光体はＬＥＤ放射による照射時に白色光を放出すべきである。
【００１９】
さらに、２種類以上の蛍光体を使用することで、白色光の色特性を所望の色パラメーターに適合するように変化させることができる。例えば、特定の蛍光体を特定の比率で選択することで、白色光の色温度及びＣＲＩ又は装置の視感度を最適化することができる。例えば、北米市場で望ましい３０００～６５００Ｋの色温度、７０を上回るＣＲＩ及び３００ｌｍ／Ｗを上回る視感度を有する白色光照明装置が得られるように蛍光体比率を選択して

もよい。フラッシュライト用としては、４０００～６５００Ｋの色温度が特に望ましい。別法として、ヨーロッパ市場で望ましい３０００～４１００Ｋの色温度、９０を上回るＣＲＩ及び２００ｌｍ／Ｗを上回る視感度を有する白色光照明装置が得られるように他の蛍光体比率を選択してもよい。

【００２０】

本発明者等は、約５７５～６２０ｎｍの範囲内にピーク発光波長を有する第１の橙色発光蛍光体、約４９５～約５５０ｎｍの範囲内にピーク発光波長を有する第２の青緑色発光蛍光体、及び約４２０～約４８０のピーク発光波長を有する第３の青色発光蛍光体を併用すると、観察者はこれらの複合発光を白色光として感知することを見出した。さらに、照明装置のＣＲＩを高めるため、約６２０～約６７０のピーク発光波長を有する第４の赤色発光蛍光体を任意成分として添加してもよい。

【００２１】

図２は上記の原理を模式的に示す。図２では、ＬＥＤのような放射源１から放出された放射２が、３種類の発光材料層３（例えば、上記のような第１、第２及び第３の蛍光体）に入射する。放射２は、人間の目が感じない波長（例えば、４２０ｎｍ以下の波長）を有し得る。別法では、蛍光体３は有意の放射２を反対側に通過させない程度の厚さを有し得る。入射した放射２を吸収した後、第１の蛍光体は５７５～６２０ｎｍの範囲内にピーク発光波長を有する橙色光４を放出し、第２の蛍光体は４９５～５５０ｎｍの範囲内にピーク発光波長を有する青緑色光５を放出し、第３の蛍光体は４２０～４８０ｎｍの範囲内にピーク発光波長を有する青色光６を放出する。第４の蛍光体が存在する場合、６２０～６７０ｎｍの範囲内にピーク発光波長を有する赤色光７を放出する。観察者８は、橙色光４、青緑色光５、青色光６及び任意要素の赤色光７の組合せを白色光９として感知する。図２は、混色の概念を例示するため、異なる色の光４、５、６及び７が別個の蛍光体領域から発生することを模式的に示す。ただし、各蛍光体を混合して単一の混合蛍光体層３を形成すれば、光４、５、６及び７が同一領域及び／又は蛍光体全体から放出されるようになる。

【００２２】

蛍光体やシンチレーターのような発光材料を放射源と併用することで、白色光照明装置を形成することができる。なお、発光材料は放射源の特定の発光波長で高い量子効率を有するのが好ましい。さらに、各々の発光材料は他の発光材料から放出される可視光波長に対して透明であるのが好ましい。

【００２３】

１．<u>放射源</u>

放射源１は、蛍光体からの発光を生起させることのできる放射源からなるものであればよい。好ましくは、放射源１はＬＥＤからなる。ただし、放射源１は蛍光ランプ又は高圧水銀灯中の水銀などのガス或いはプラズマディスプレイ中のＮｅ、Ａｒ及び／又はＸｅなどの貴ガスからなるものでもよい。

【００２４】

放射源１は、例えば、ＬＥＤから放出された放射２が蛍光体に入射したときに蛍光体３から観察者８に白く見える放射９を放出させるＬＥＤからなるものであればよい。例えば、ＬＥＤは適宜ＩＩＩ－Ｖ、ＩＩ－ＶＩ又はＩＶ－ＩＶ半導体層を基材とし、３６０～４２０ｎｍの発光波長を有する半導体ダイオードからなるものでよい。例えば、ＬＥＤはＧａＮ、ＺｎＳｅ又はＳｉＣ半導体を基材とする１以上の半導体層を含むものでもよい。また、所望に応じて、ＬＥＤは活性領域内に１以上の量子井戸を含んでいてもよい。好ましくは、ＬＥＤの活性領域はＧａＮ、ＡｌＧａＮ及び／又はＩｎＧａｎ半導体層からなるｐ－ｎ接合を含んでいてもよい。ｐ－ｎ接合は、薄い非ドープＩｎＧａｎ層又は１以上のＩｎＧａｎ量子井戸で隔離してもよい。ＬＥＤは、３６０～４２０ｎｍの範囲内、好ましくは３７０～４０５ｎｍの範囲内、最も好ましくは３７０～３９０ｎｍの範囲内に発光波長を有し得る。ただし、発光波長が４２０ｎｍよりも長いＬＥＤを、ＬＥＤからの放出光が蛍光体を通過しないような厚さの厚い蛍光体と併用してもよい。例えば、ＬＥＤは３７０、

３７５、３８０、３９０又は４０５ｎｍのような波長を有し得る。

【００２５】

以上、白色光照明装置の放射源１については半導体発光ダイオードとして説明してきた。ただし、本発明の放射源は半導体発光ダイオードのみに限定されない。例えば、放射源はレーザーダイオード又は有機発光ダイオード（ＯＬＥＤ）からなるものでもよい。上記の好ましい白色光照明装置は単一の放射源１を含む。ただし、放出される白色光を改善したり或いは放出される白色光を異なる色の光と混合するため、所望に応じて装置内に複数の放射源を使用してもよい。例えば、ディスプレイ装置内で白色光照明装置を赤色、緑色及び／又は青色発光ダイオードと併用してもよい。

【００２６】

２．第１の蛍光体

第１の発光材料は、放射源１からの入射放射２に応答して約５７５～約６２０ｎｍのピーク発光波長を有する可視光を放出する蛍光体であればよい。放射源１が３６０～４２０ｎｍの範囲内にピーク発光波長を有するＬＥＤからなる場合、第１の蛍光体は、３６０～４２０ｎｍの範囲内にピーク波長を有する入射放射に対して５７５～６２０ｎｍの範囲内にピーク発光波長並びに高い相対視感度及び量子効率を有する商業的に入手可能な蛍光体からなるものであればよい。

【００２７】

好ましくは、第１の蛍光体は$APO:Eu^{2+},Mn^{2+}$（式中、ＡはＳｒ、Ｃａ、Ｂａ及びＭｇの１種以上を含む）を含む。最も好ましくは、第１の蛍光体はユウロピウム及びマンガンをドープしたピロリン酸アルカリ土類金属塩蛍光体$A_2P_2O_7:Eu^{2+},Mn^{2+}$を含む。かかる蛍光体は、$(A_{1-x-y}Eu_xMn_y)_2P_2O_7$（式中、$0<x\leqq 0.2$、$0<y\leqq 0.2$）と書くことができる。好ましくは、Ａはストロンチウムイオンである。この蛍光体は、ＬＥＤから放出される３６０～４２０ｎｍの範囲内にピーク波長を有する入射放射に対して高い視感度及び高い量子効率を有するので、ＬＥＤ放射源用として好ましい。別法として、第１の蛍光体は$A_3P_2O_8:Eu^{2+},Mn^{2+}$（式中、ＡはＳｒ、Ｃａ、Ｂａ及びＭｇの１種以上を含む）からなるものでもよい。

【００２８】

Eu^{2+}及びMn^{2+}をドープしたピロリン酸アルカリ土類金属塩蛍光体では、Ｅｕイオンは一般に増感剤として作用し、Ｍｎイオンは一般に活性化剤として作用する。すなわち、Ｅｕイオンは放射源から放出された入射エネルギー（すなわち、光子）を吸収し、吸収エネルギーをＭｎイオンに伝達する。Ｍｎイオンは吸収・伝達されたエネルギーによって励起状態に高められ、ＡイオンがＳｒイオンからなるときは約５７５ｎｍから５９５ｎｍまで変化するピーク波長をもつ幅の広い放射バンドを放出する。別法として、Ａは５０モル％のＳｒイオンと５０モル％のＭｇイオンからなるものとし、$APO:Eu^{2+},Mn^{2+}$蛍光体が約６１５ｎｍのピーク波長を有する$SrMgP_2O_7:Eu^{2+},Mn^{2+}$蛍光体となるようにしてもよい。

【００２９】

３．第２の蛍光体

第２の発光材料は、放射源１からの入射放射２に応答して約４９５～約５５０ｎｍのピーク発光波長を有する可視光を放出する蛍光体であればよい。放射源１が３６０～４２０ｎｍの範囲内にピーク発光波長を有するＬＥＤからなる場合、第２の蛍光体は、３６０～４２０ｎｍの範囲内にピーク波長を有する入射放射に対して４９５～５５０ｎｍの範囲内にピーク発光波長並びに高い相対視感度及び量子効率を有する商業的に入手可能な蛍光体からなるものであればよい。例えば、下記の３種類のEu^{2+}活性化ケイ酸アルカリ土類金属塩及びアルミン酸アルカリ土類金属塩蛍光体がこの基準に適合する。

【００３０】

かかる蛍光体の一つは、二価ユウロピウムで活性化されたケイ酸アルカリ土類金属塩蛍光体$ASiO:Eu^{2+}$（式中、ＡはＢａ、Ｃａ、Ｓｒ及びＭｇの１種以上を含む）である。好ましくは、$ASiO:Eu^{2+}$蛍光体は組成$A_2SiO_4:Eu^{2+}$を有し、Ａは好

ましくは６０％以上のＢａ、３０％以下のＳｒ、及び１０％以下のＣａからなる。ＡがＢａ又はＣａからなる場合、蛍光体のピーク発光波長は約５０５ｎｍである。ＡがＳｒからなる場合、蛍光体のピーク発光波長は約５８０ｎｍである。従って、所望のピーク波長を得るため、Ａは最も好ましくはＢａイオンのみ或いは少量のＣａ及び／又はＳｒイオンを含むＢａイオンからなる。

【００３１】

ケイ酸アルカリ土類金属塩蛍光体では、ユウロピウム活性化剤はアルカリ土類金属の格子部位を置換するので、蛍光体は$((Ba,Sr,Ca)_{1-x}Eu_x)_2SiO_4$（式中、$0<x\leq 0.2$）と書くことができる。ケイ酸アルカリ土類金属塩蛍光体はその他の不純物及びドーパントを含んでいてもよい。例えば、蛍光体は粉末加工中にフッ素含有フラックス化合物（例えば、BaF_2又はEuF_3）から混入した少量のフッ素を含んでいてもよい。

【００３２】

その他の二価ユウロピウムで活性化されたケイ酸アルカリ土類金属塩蛍光体$ADSiO:Eu^{2+}$（式中、ＡはＢａ、Ｃａ及びＳｒの１種以上を含み、ＤはＭｇ及びＺｎの１種以上を含む）も第２の蛍光体として適している。好ましくは、$ADSiO:Eu^{2+}$蛍光体は組成$A_2DSi_2O_7:Eu^{2+}$を有する。各同形蛍光体のピーク発光波長及び相対量子効率を下記の表Ｉに示す。

【００３３】

【表１】

表Ｉ

	A	D	A	D	A	D	A	D	A	D	A	D
	Ca	Mg	Sr	Mg	Sr	Zn	Sr/Ba	Mg	Ba	Mg	Ba	Zn
ピークλ	535		470		470		440		500		505	

【００３４】

従って、所望のピーク波長を得るため、Ａは最も好ましくはＢａイオンのみ或いは少量のＣａ又はＳｒイオンを含むＢａイオンからなる。

【００３５】

ケイ酸アルカリ土類金属塩蛍光体では、ユウロピウム活性化剤はアルカリ土類金属の格子部位を置換するので、蛍光体は$(A_{1-x}Eu_x)_2DSiO_7$（式中、$0<x\leq 0.2$）と書くことができる。ケイ酸アルカリ土類金属塩蛍光体はその他の不純物及びドーパントを含んでいてもよい。例えば、かかる蛍光体は粉末加工中にフッ素含有フラックス化合物（例えば、BaF_2又はEuF_3）から混入した少量のフッ素を含んでいてもよい。

【００３６】

また、二価ユウロピウムで活性化されたアルミン酸アルカリ土類金属塩蛍光体$AAlO:Eu^{2+}$（式中、ＡはＢａ、Ｓｒ及びＣａの１種以上を含む）も第２の蛍光体として用いるのに適している。好ましくは、$AAlO:Eu^{2+}$蛍光体は組成$AAl_2O_4:Eu^{2+}$を有し、Ａは５０％以上のＳｒからなり、好ましくは８０％以上のＳｒ及び２０％以下のＢａからなる。ＡがＳｒからなる場合、蛍光体のピーク発光波長は約５０５ｎｍである。ＡがＳｒからなる場合、蛍光体のピーク発光波長は約５２０ｎｍである。ＡがＣａからなる場合、蛍光体のピーク発光波長は約４４０ｎｍである。従って、所望のピーク波長を得るため、Ａは最も好ましくはＳｒイオン或いはＳｒ及びＢａイオンからなる。

【００３７】

アルミン酸アルカリ土類金属塩蛍光体では、ユウロピウム活性化剤はアルカリ土類金属の格子部位を置換するので、蛍光体は$(A_{1-x}Eu_x)_2Al_2O_4$（式中、０＜ｘ≦０

．２）と書くことができる。アルミン酸アルカリ土類金属塩蛍光体はその他の不純物及びドーパント（例えば、フラックスから混入したフッ素）を含んでいてもよい。

【００３８】

ユウロピウムで活性化されたケイ酸アルカリ土類金属塩蛍光体は、Ｇ．Ｂｌａｓｓｅ他，“Ｆｌｕｏｒｅｓｃｅｎｃｅ ｏｆ Eu^{2+} Ａｃｔｉｖａｔｅｄ Ｓｉｌｉｃａｔｅｓ” ２３ Ｐｈｉｌｉｐｓ Ｒｅｓ． Ｒｅｐｔｓ．，１８９～２００（１９６８）（その記載内容は援用によって本明細書の一部をなす）に詳細に記載されている。ユウロピウムで活性化されたアルミン酸アルカリ土類金属塩蛍光体は、Ｇ．Ｂｌａｓｓｅ他，“Ｆｌｕｏｒｅｓｃｅｎｃｅ ｏｆ Eu^{2+} Ａｃｔｉｖａｔｅｄ Ａｌｋａｌｉｎｅ－Ｅａｒｔｈ Ａｌｕｍｉｎａｔｅｓ” ２３ Ｐｈｉｌｉｐｓ Ｒｅｓ． Ｒｅｐｔｓ．，２０１～２０６（１９６８）（その記載内容は援用によって本明細書の一部をなす）に詳細に記載されている。これらの刊行物には、上述の蛍光体の発光及び励起スペクトルも例示されている。

【００３９】

本発明の一態様では、色又はその他の発光特性を最適化するため、第２の蛍光体は所望に応じて複数のケイ酸塩及びアルミン酸塩蛍光体からなるものであってもよい。例えば、第２の蛍光体はＡＳｉＯ：Eu^{2+}とＡＤＳｉＯ：Eu^{2+}との組合せ、ＡＳｉＯ：Eu^{2+}とＡＡｌＯ：Eu^{2+}との組合せ、ＡＤＳｉＯ：Eu^{2+}とＡＡｌＯ：Eu^{2+}との組合せ、或いはＡＳｉＯ：Eu^{2+}とＡＤＳｉＯ：Eu^{2+}とＡＡｌＯ：Eu^{2+}の組合せでよい。上記の蛍光体は、重なり合った層又はブレンドとして同じ照明装置内に配置し得る。

【００４０】

４．第３の蛍光体

第３の発光材料は、放射源１からの入射放射２に応答して約４２０～約４８０ｎｍのピーク発光波長を有する可視光を放出する蛍光体であればよい。放射源１が３６０～４２０ｎｍの範囲内にピーク発光波長を有するＬＥＤからなる場合、第３の蛍光体は、３６０～４２０ｎｍの範囲内にピーク波長を有する入射放射に対して４２０～４８０ｎｍの範囲内にピーク発光波長並びに高い視感度及び量子効率を有する商業的に入手可能な蛍光体からなるものであればよい。例えば、下記の２種類の商業的に入手可能なEu^{2+}活性化蛍光体がこの基準に適合する。

【００４１】

４２０～４８０ｎｍの範囲内にピーク発光波長を有する第３の蛍光体の一例は、二価ユウロピウムで活性化されたハロリン酸塩蛍光体ＤＰＯＣｌ：Eu^{2+}（式中、ＤはＳｒ、Ｂａ、Ｃａ及びＭｇの１種以上を含む）である。ＤＰＯＣｌ：Eu^{2+}蛍光体は、商業的に入手可能な「ＳＥＣＡ」蛍光体$D_5(PO_4)_3Cl:Eu^{2+}$からなるのが好ましい。発光強度を高めるため、少量のリン酸塩を少量のホウ酸塩で置換してもよい。この蛍光体のピーク発光波長は、ストロンチウムイオンと他のアルカリ土類金属イオンとの比率に応じて変化する。ＤがＳｒイオンのみからなる場合、ピーク発光波長は４４７ｎｍである。ＳｒイオンをＢａイオンで置換すればピーク発光が短波長側に移動し、ＳｒイオンをＣａイオンで置換すればピーク発光が長波長側に移動する。例えば、５モルのＳｒイオンのうち０．５モルを０．５モルのＣａイオンで置換すると、ピーク発光は４５２ｎｍに移動する。１モルのＳｒイオンを０．５モルのＣａイオン及び０．５モルのＢａイオンで置換すると、ピーク発光は４４５ｎｍに移動する。従って、好ましいＳＥＣＡ蛍光体組成は$(Sr_{1-y-z}Ba_yCa_z)_{5-x}Eu_x(PO_4)_3Cl$（式中、$0.01 \leqq x \leqq 0.2$、$0 \leqq y \leqq 0.1$、$0 \leqq z \leqq 0.1$）であり、好ましいピーク発光波長は４４７～４５０ｎｍである。

【００４２】

４２０～４８０ｎｍの範囲内にピーク発光波長を有する第３の蛍光体の別の例は、二価ユウロピウムで活性化されたアルミン酸アルカリ土類金属塩蛍光体ＡＭｇＡｌＯ：Eu^{2+}（式中、ＤはＢａ、Ｃａ及びＳｒの１種以上を含む）である。好ましいアルミン酸塩蛍光

体は様々なマグネシウム、アルミニウム及び酸素のモル比を有し、「ＢＡＭ」の名称で商業的に入手することができる。例えば、好ましいＢＡＭ蛍光体の一つは$AMg_2Al_{16}O_{27}:Eu^{2+}$（式中、Ａは９０％以上のＢａイオンを含むのが好ましい）と書くことができる。この蛍光体は組成$(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$（式中、$0\leqq x\leqq 0.2$であり、好ましくは$x=0.07$である）を有する。別法として、ＢＡＭはモル比$BaMgAl_{10}O_{17}:Eu^{2+}$を有する。ＢＡＭ蛍光体は、Ａの格子部位に$Eu^{2+}$活性化剤が存在するため、約４５０ｎｍに発光ピークを有する。ストロンチウムイオンでのバリウムイオン置換量の増加に伴って、発光ピークは４５０ｎｍから長波長側に移動する。

【００４３】

４２０～４８０ｎｍの範囲内にピーク発光波長を有する第３の蛍光体の別の例は、$EO*AlO:Eu^{2+}$蛍光体、$EAlO:Eu^{2+}$蛍光体及び／又は$GAlO:Eu^{2+}$蛍光体（式中、ＥはＢａ、Ｓｒ及びＣａイオンの１種以上からなり、ＧはＫ、Ｌｉ、Ｎａ及びＲｂイオンの１種以上を含む）から選択される二価ユウロピウム活性化アルミン酸塩蛍光体を含む。好ましくは、Ｅは０～１０％のＳｒ又はＣａイオンで置換されたＢａイオンからなり、Ｇは０～１０％のＬｉ、Ｎａ又はＲｂイオンで置換されたＫを含む。好ましくは、$EO*AlO:Eu^{2+}$蛍光体は$z(BaO)*6Al_2O_3:Eu^{2+}$又は$z(Ba_{1-x}Eu_x)O*6Al_2O_3$（式中、$1\leqq z\leqq 1.8$、$0\leqq x\leqq 0.2$）を含む。$EAlO:Eu^{2+}$蛍光体は$BaAl_{12}O_{19}:Eu^{2+}$又は$(Ba_{1-x}Eu_x)Al_{12}O_{19}$（式中、$0\leqq x\leqq 0.2$）を含むのが好ましい。$GAlO:Eu^{2+}$蛍光体は$KAl_{11}O_{11.07}:Eu^{2+}$又は$(K_{1-x}Eu_x)Al_{11}O_{11.07}$（式中、$0\leqq x\leqq 0.2$）を含むのが好ましい。ＥＯ＊ＡｌＯ、ＥＡｌＯ及びＧＡｌＯ蛍光体は、以下の参考文献：Ａ．Ｌ．Ｎ．Ｓｔｅｖｅｌ及びＡ．Ｄ．Ｍ．Ｓｃｈｒａｍａ－ｄｅ Ｐａｕｗ，Ｊｏｕｒｎａｌ ｏｆ ｔｈｅ Ｅｌｅｃｔｒｏｃｈｅｍｉｃａｌ Ｓｏｃｉｅｔｙ，１２３（１９７６）６９１、Ｊ．Ｍ．Ｐ．Ｊ．Ｖｅｒｓｔｅｇｅｎ，Ｊｏｕｒｎａｌ ｏｆ ｔｈｅ Ｅｌｅｃｔｒｏｃｈｅｍｉｃａｌ Ｓｏｃｉｅｔｙ、１２１（１９７４）１６２３、並びにＣ．Ｒ．Ｒｏｎｄａ及びＢ．Ｍ．Ｊ．Ｓｍｅｔｓ，Ｊｏｕｒｎａｌ ｏｆ ｔｈｅ Ｅｌｅｃｔｒｏｃｈｅｍｉｃａｌ Ｓｏｃｉｅｔｙ、１３６（１９８９）５７０に記載されており、その記載内容は援用によって本明細書の一部をなす。

【００４４】

本発明の一態様では、第２の蛍光体は、色又はその他の発光特性を最適化するため、所望に応じて、ＳＥＣＡ、ＢＡＭ及び／又は１種以上のアルミン酸塩蛍光体のブレンドからなるものでもよい。

【００４５】

５．<u>任意の第４の蛍光体</u>

任意成分としての第４の発光材料は、放射源１からの入射放射２に応答して約６２０～約６７０ｎｍのピーク発光波長を有する可視光を放出する蛍光体であればよい。赤色発光蛍光体は、蛍光体の組合せから放出される白色光のＣＲＩを改善するため、第１、第２及び第３の蛍光体に添加してもよい。ＣＲＩは蛍光体からの照明下での試験色が黒体からの照明下と比較してどのように見えるかを示す尺度であるから、蛍光体の発光が個々の色をさらに含むと、蛍光体からの白色光は黒体からの白色光に一段と近づく。放射源１が３６０～４２０ｎｍの範囲内にピーク発光波長を有するＬＥＤからなる場合、第２の蛍光体は、３６０～４２０ｎｍの範囲内にピーク波長を有する入射放射に対して６２０～６７０ｎｍの範囲内にピーク発光波長並びに高い視感度及び量子効率を有する商業的に入手可能な蛍光体からなるものであればよい。例えば、Mn^{4+}で活性化されたフルオロゲルマニウム酸塩蛍光体がこの基準に適合する。

【００４６】

例えば、フルオロゲルマニウム酸塩蛍光体はフルオロゲルマニウム酸マグネシウム蛍光体$MgO*MgF*GeO:Mn^{4+}$（好ましくは、商業的に入手可能な３．５ＭｇＯ＊０

．５MgF_2＊GeO_2：Mn^{4+}蛍光体）を含むものでもよい。この蛍光体は、６２３～６６４ｎｍの間に室温で６つのピークを有する構造化赤色発光バンドを放出する。

【００４７】

６．蛍光体ブレンド

本発明の好ましい一態様によれば、第１、第２、第３、及び任意成分の第４の蛍光体は散在している。最も好ましくは、これらの蛍光体は均質なブレンドを生ずるように混合される。ブレンド中の各蛍光体の量は、蛍光体の種類及び用いられ放射源の種類に依存する。ただし、第１、第２、第３、及び任意成分の第４の蛍光体は、蛍光体からの発光９の組合せが観察者８に白く見えるようにブレンドすべきである。

【００４８】

別法として、第１、第２、第３、及び任意成分の第４の蛍光体は放射源１上に形成された別個の層をなすこともできる。ただし、上方の蛍光体層は下方の蛍光体から放出される放射に対して実質的に透明とすべきである。

【００４９】

蛍光体粉末ブレンドの組成は、使用する蛍光体の数、所望のブレンドＣＲＩ及び視感度、蛍光体の組成、並びに放射源１のピーク発光波長に基づいて最適化し得る。例えば、一定の励起放射波長に対する蛍光体ブレンドの色温度を低下させるため、青色乃至橙色発光蛍光体の比率を下げてもよい。蛍光体ブレンドのＣＲＩを高めるため、赤色発光蛍光体のような第４の蛍光体をブレンドに添加してもよい。

【００５０】

本発明の第１の好ましい態様に係る蛍光体ブレンドは、好ましくは３種類以上の蛍光体を含み、３６０～４２０ｎｍの範囲内にピーク波長を有する入射放射又は励起放射に応答して蛍光体ブレンドから放出される白色光は３０００～６５００Ｋの範囲内の色温度、７０を上回るＣＲＩ、及び２００ｌｍ／Ｗを上回る視感度を有する。さらに好ましくは、ブレンドの視感度は２６４ｌｍ／Ｗを上回り、色温度は３３００～４１００Ｋの範囲内にある。最も好ましくは、視感度は２６４ｌｍ／Ｗを上回る。

【００５１】

本発明の第１の好ましい態様に係る好ましい第１、第２及び第３の蛍光体は、それぞれピロリン酸ストロンチウム、ケイ酸アルカリ土類金属塩及びＳＥＣＡである。第１の好ましい態様に係るブレンドの組成は、約５５～約７５重量％の$Sr_2P_2O_7$：Eu^{2+}，Mn^{2+}蛍光体、約１１～約２２重量％の$(Ba,Sr,Ca)_2SiO_4$：Eu^{2+}蛍光体、及び約１３～約２２重量％の$(Sr,Ba,Ca,Mg)_5(PO_4)_3Cl$：$Eu^{2+}$蛍光体を含む。

【００５２】

本発明の第２の好ましい態様に係る高ＣＲＩの蛍光体ブレンドは、好ましくは４種類以上の蛍光体を含み、３６０～４２０ｎｍの範囲内にピーク波長を有する入射放射に応答して蛍光体ブレンドから放出される白色光は３０００～４１００Ｋの範囲内の色温度、９０を上回るＣＲＩ、及び２００ｌｍ／Ｗを上回る視感度を有する。さらに好ましくは、ブレンドの視感度は２６４ｌｍ／Ｗを上回り、色温度は３３００～３８００Ｋの範囲内にある。

【００５３】

本発明の第２の好ましい態様に係る好ましい第１、第２、第３及び第４の蛍光体は、それぞれピロリン酸ストロンチウム、ケイ酸アルカリ土類金属塩、ＳＥＣＡ及びフルオロゲルマニウム酸マグネシウムである。第２の好ましい態様に係るブレンドの組成は、約１１～約４３重量％の$Sr_2P_2O_7$：Eu^{2+}，Mn^{2+}蛍光体、約９～約１５重量％の$(Ba,Sr,Ca)_2SiO_4$：Eu^{2+}蛍光体、約６～約１４重量％の$(Sr,Ba,Ca,Mg)_5(PO_4)_3Cl$：$Eu^{2+}$蛍光体、及び約３０～約７１重量％の３．５$MgO$＊０．５$MgF_2$＊$GeO_2$：$Mn^{4+}$蛍光体を含む。

【００５４】

ただし、上記の蛍光体の代りに、或いは上記の蛍光体に加えて、所望のピーク発光波長を有するその他の蛍光体を使用してもよい。例えば、ＬＥＤ以外の放射源に対しては、２５

４ｎｍ及び１４７ｎｍのピーク波長を有する入射放射に対して高い視感度及び高い量子効率を有する蛍光体をそれぞれ蛍光ランプ及びプラズマディスプレイ用途に使用し得る。蛍光ランプでの水銀ガス発光は２５４ｎｍのピーク発光波長を有し、プラズマディスプレイでのＸｅプラズマ放電は１４７ｎｍのピーク発光波長を有する。

【００５５】

７．照明装置

本発明の第１の好ましい実施形態によれば、第１、第２、第３及び任意成分の第４の蛍光体粉末は、ＬＥＤ放射源を含む白色光照明装置内に配置される。かかる白色光照明装置は多種多様な構造を有し得る。

【００５６】

第１の好ましい構造を図３に略示する。かかる照明装置は、発光ダイオードチップ１１及びＬＥＤチップに電気的に取付けられたリード線１３を含む。リード線１３は厚いリードフレーム１５で支持された細線からなるものでもよいし、或いはリード線が自立性の電極をなしていて、リードフレームを省くこともできる。リード線１３はＬＥＤチップ１１に電流を供給し、ＬＥＤチップ１１から放射を放出させる。

【００５７】

ＬＥＤチップ１１はシェル１７の内部に封入され、シェル１７はＬＥＤチップ及び封入材料１９を囲む。好ましくは、封入材料は耐紫外線性エポキシ樹脂からなる。シェル１７は、例えばガラス又はプラスチックでよい。封入材料は、例えばエポキシ樹脂又はシリコーンのような高分子物質でよい。ただし、独立シェル１７をなくし、封入材料１９の外面がシェル１７をなすようにしてもよい。ＬＥＤチップ１１は、例えば、リードフレーム１５、自立性の電極、シェル１７の底部、或いはシェル又はリードフレームに取付けられた台座で支持し得る。

【００５８】

照明装置の第１の好ましい構造は、第１、第２、第３及び任意成分の第４の蛍光体からなる蛍光体層２１を含む。蛍光体層２１は、第１、第２、第３及び任意成分の第４の蛍光体粉末を含有する懸濁液をＬＥＤチップ１１に塗布して乾燥することによって、ＬＥＤチップ１１の発光面の上方又は発光面上に直接形成し得る。乾燥後、蛍光体粉末は固形の蛍光体層又は被膜２１を形成する。シェル１７及び封入材料１９はいずれも、白色光２３がこれらの要素を通過し得るように透明とすべきである。蛍光体は、第１、第２、第３及び任意成分の第４の蛍光体からそれぞれ放出された橙色光、青緑色光、青色光及び任意成分の赤色光からなる白色光２３を放出する。

【００５９】

図４は、本発明の第１の好ましい実施形態に係る装置の第２の好ましい構造を示す。ＬＥＤチップ１１上に蛍光体層を形成する代りに蛍光体粉末を封入材料１９の内部に散在させた点を除けば、図４の構造は図３のものと同じである。第１の蛍光体粉末は、封入材料１９の単一領域内に散在させることもできるし、或いは封入材料の全体積にわたって散在させることもできる。封入材料の内部に蛍光体粉末を散在させるには、例えば、重合体前駆物質に粉末を添加し、次いで重合体前駆物質を硬化させて高分子物質を固化させればよい。別法として、エポキシ樹脂封入材料中に蛍光体粉末を混入してもよい。その他の蛍光体散在方法も使用し得る。蛍光体粉末を予備混合してから粉末混合物を封入材料１９に添加してもよいし、或いは蛍光体粉末を別個に封入材料１９に添加してもよい。別法として、所望に応じて、第１、第２、第３及び任意成分の第４の蛍光体からなる固形の蛍光体層２１を封入材料１９中に挿入してもよい。かかる構造では、蛍光体層２１はＬＥＤから放出された放射２５を吸収し、それに応答して白色光２３を放出する。

【００６０】

図５は、本発明の第１の好ましい実施形態に係る装置の第３の好ましい構造を示す。ＬＥＤチップ１１上に蛍光体層を形成する代りに、第１、第２、第３及び任意成分の第４の蛍光体を含む蛍光体層２１をシェル１７上に形成した点を除けば、図５の構造は図３のものと同じである。蛍光体層２１はシェル１７の内面に形成するのが好ましいが、所望に応じ

て、蛍光体層２１をシェルの外面に形成してもよい。蛍光体層２１は、シェルの全表面に形成してもよいし、或いはシェル１７の表面の頂部のみに形成してもよい。
【００６１】
もちろん、図３～５の実施形態を組合わせてもよいし、蛍光体をいずれか２箇所又は３箇所すべて或いはその他の位置に配置してもよく、例えばシェルから分離して配置しても、ＬＥＤに組込んでもよい。
【００６２】
本発明の第２の好ましい実施形態によれば、第１、第２、第３及び任意成分の第４の粉末は、蛍光ランプ放射源を含む白色光照明装置内に配置される。蛍光ランプの一部分を図６に略示する。ランプ３１は、第１、第２、第３及び任意成分の第４の蛍光体からなる蛍光体被膜３５をランプカバー３３の表面（好ましくは内面）に含む。また、蛍光ランプ３１はランプ口金３７及び陰極３９を含むのが好ましい。ランプカバー３３は、陰極３９に印加された電圧に応答して紫外線を放出するガス（例えば、水銀）を収容している。
【００６３】
本発明の第３の好ましい実施形態によれば、第１、第２、第３及び任意成分の第４の蛍光体粉末は、プラズマディスプレイ装置を含む白色光照明装置内に配置される。Ｓ．Ｓｈｉｏｎｏｙａ及びＷ．Ｍ．Ｙｅｎ編，“Ｐｈｏｓｐｈｏｒ　Ｈａｎｄｂｏｏｋ”（ＣＲＣ　Ｐｒｅｓ，１９８７，１９９９）６２３～６３９頁（その記載内容は援用によって本明細書の一部をなす）に記載されている装置のようなＡＣ又はＤＣプラズマディスプレイパネルなど、あらゆるプラズマディスプレイ装置を使用し得る。図７は、ＤＣプラズマディスプレイ装置４１の一つのセルを略示したものである。セルは、第１のガラス板４２、第２のガラス板４３、１以上の陰極４４、１以上の陽極４５、第１、第２、第３及び任意成分の第４の蛍光体からなる蛍光体層４６、バリヤーリブ４７並びに貴ガス空間４８を含む。ＡＣプラズマディスプレイ装置では、陰極とガス空間４８との間に追加の誘電体層が設けられる。陽極４５と陰極４４との間に電圧を印加すると、空間４８内の貴ガスが短波長の真空紫外線（ＶＵＶ）を放出し、蛍光体層４６を励起して白色光を放出させる。
【００６４】
８．<u>加工方法</u>
各々の蛍光体は、例えばどんなセラミック粉体法（例えば、湿式化学法又は固相法）で製造してもよい。
【００６５】
好ましくは、ユウロピウム及びマンガンをドープしたピロリン酸ストロンチウム蛍光体からなる第１の蛍光体の製造方法は、以下の工程を含む。最初に、第１の蛍光体の原料化合物をるつぼ内で手作業でブレンド又は混合するか、或いは別の適当な容器（例えば、ボールミル）内で機械的にブレンド又は混合して原料粉末混合物を調製する。原料化合物は、どんな酸化物、リン酸塩、水酸化物、シュウ酸塩、炭酸塩及び／又は硝酸塩系蛍光体原料化合物からなるものでもよい。好ましい蛍光体原料化合物としては、リン酸水素ストロンチウム（$SrHPO_4$）、炭酸マンガン（$MnCO_3$）、酸化ユウロピウム（Eu_2O_3）及びリン酸水素アンモニウム（$(NH_4)HPO_4$）粉末が挙げられる。$(NH_4)HPO_4$粉末は、好ましくは、生成する第１の蛍光体１モル当り化学量論比の２％過剰量で添加される。また、所望に応じて、若干過剰量のＳｒ化合物を添加してもよい。また、ストロンチウムの一部又は全部をカルシウム、バリウム及び／又はマグネシウムで置換するのが望まれる場合、カルシウム、バリウム及びマグネシウム原料化合物を添加してもよい。次に、原料粉末混合物を約３００～８００℃（好ましくは６００℃）の空気中で約１～５時間加熱する。次に、得られた粉末を再度ブレンドし、次いで約１０００～１２５０℃（好ましくは１０００℃）の還元雰囲気中で焼成して、焼成蛍光体塊又はケークを得る。好ましくは、窒素及び０．１～１０％の水素からなる雰囲気の炉内で原料雰囲気混合物を４～１０時間（好ましくは８時間）焼成し、次いで炉の電源を切って同じ雰囲気中で冷却する。
【００６６】

好ましくは、第2の好ましい（Ｂａ：Ｓｒ，Ｃａ）$_2$ＳｉＯ$_4$：Ｅｕ$^{2+}$蛍光体の製造方法は、以下の工程を含む。まず、蛍光体の原料化合物をるつぼ内で手作業でブレンド又は混合するか、或いは別の適当な容器（例えば、ボールミル）内で機械的にブレンド又は混合して、原料粉末混合物を調製する。原料化合物は、どんな酸化物、水酸化物、シュウ酸塩、炭酸塩及び／又は硝酸塩系蛍光体原料化合物からなるものでもよい。好ましい蛍光体原料化合物としては、炭酸バリウム（ＢａＣＯ$_3$）、炭酸ストロンチウム（ＳｒＣＯ$_3$）、炭酸カルシウム（ＣａＣＯ$_3$）、酸化ユウロピウム（Ｅｕ$_2$Ｏ$_3$）及びケイ酸（ＳｉＯ$_2$＊ｘＨ$_2$Ｏ）が挙げられる。好ましくは、生成蛍光体１モル当り０．５～３モル％量のＣａＦ$_2$などのフラックスを添加する。次に、まず１２００～１４００℃の炭素含有雰囲気（例えば、木炭含有雰囲気）中で原料粉末混合物を５～７時間焼成して、第１の焼成蛍光体塊又はケークを得る。次いで、得られたケークを粉砕及び摩砕して粉末とする。この粉末を次に約９００～１２００℃の還元雰囲気中でアニール又は焼成して、第２の焼成蛍光体塊又はケークを得る。好ましくは、窒素及び０．１～１０％の水素からなる雰囲気の炉内で粉末を２～６時間アニールする。

【００６７】

固形焼成蛍光体塊を第１蛍光体粉末に粉砕して、蛍光体粉末が白色光照明装置の一部に容易に塗布できるようにしてもよい。固形蛍光体塊を第１蛍光体粉末にするには、適宜、破砕、摩砕又は微粉砕法（例えば、湿式摩砕、乾式摩砕、ジェットミリング又は破砕）を用いればよい。好ましくは、固形塊をプロパノール、メタノール及び／又は水中での湿式摩砕に付し、乾燥する。

【００６８】

第３及び第４の蛍光体は蛍光体粉末として商業的に入手可能であり、その正確な製造方法は重要でない。ＢＡＭ及びＳＥＣＡ蛍光体の合成法は、Ｓ．Ｓｈｉｏｎｏｙａ他編，“Ｐｈｏｓｐｈｏｒ Ｈａｎｄｂｏｏｋ”（ＣＲＣ Ｐｒｅｓｓ，１９８７，１９９９）３９８～３９９頁及び４１６～４１９頁に記載されており、その記載内容は援用によって本明細書の一部をなす。一般に、商用ＢＡＭ蛍光体の製造方法では、炭酸バリウム、炭酸マグネシウム、アルミナ又は水酸化アルミニウム、酸化ユウロピウム及び任意成分のフラックス（例えば、フッ化アルミニウム又は塩化バリウム）からなる出発原料をブレンドする。次に、約１２００～１４００℃の還元雰囲気中で原料粉末混合物を焼成して、焼成蛍光体塊又はケークを得る。ケークを同じ条件下で再粉砕し再焼成してもよい。商用ＳＥＣＡ蛍光体の製造方法では、炭酸ストロンチウム、オルトリン酸ストロンチウム、塩化ストロンチウム及び酸化ユウロピウムからなる出発原料をブレンドする。次に、約１０００～１２００℃の還元雰囲気中で原料粉末混合物を焼成して、焼成蛍光体塊又はケークを得る。次いで、ケークを粉砕すると蛍光体粉末が得られる。

【００６９】

次に、第１、第２、第３及び任意成分の第４の蛍光体粉末をブレンド又は混合して蛍光体粉末ブレンド又は混合物を調製する。粉末は、るつぼ内で手作業でブレンドしてもよいし、別の適当な容器（例えば、ボールミル）で機械的にブレンドしてもよい。蛍光体粉末ブレンドが所望に応じて５種類以上の粉末を含んでいてもよいことはいうまでもない。別法として、塊を微粉砕してブレンドしてもよい。

【００７０】

次に、蛍光体粉末ブレンドを白色光照明装置内に配置する。例えば、本発明の第１の好ましい実施形態に関して上述した通り、蛍光体粉末ブレンドをＬＥＤチップ上に配置しても、封入材料中に散在させても、或いはシェルの表面に塗布してもよい。

【００７１】

蛍光体粉末ブレンドをＬＥＤチップ又はシェルに塗布する場合には、蛍光体粉末ブレンドと液体からなる懸濁液を用いてＬＥＤチップ又はシェル表面をコートする。懸濁液は、溶剤中に溶解した結合剤を任意成分として含んでいてもよい。好ましくは、結合剤は溶剤（例えば、酢酸ブチル又はキシロール）中に溶解した有機物質（例えば、ニトロセルロース又はエチルセルロース）からなる。結合剤は、粉末粒子同士の付着力及びＬＥＤ又はシェ

ルに対する粉末粒子の付着力を高める。ただし、所望に応じて、加工を簡単にするために結合剤を省いてもよい。塗布後、懸濁液を乾燥し、加熱して結合剤を蒸発させればよい。溶剤乾燥後、蛍光体粉末ブレンドは蛍光体層２１として作用する。

【００７２】

蛍光体ブレンドを封入材料１９中に散在させる場合には、重合体前駆物質に蛍光体ブレンドを添加し、次いで重合体前駆物質を硬化させて高分子物質を固化させればよい。別法として、蛍光体ブレンドをエポキシ樹脂封入材料中に混入してもよい。その他の蛍光体散在法を使用してもよい。

【００７３】

蛍光体ブレンドを蛍光ランプ又はプラズマディスプレイ内に配置する場合には、蛍光体粉末ブレンドと液体からなる懸濁液を用いてランプ又はプラズマディスプレイの内面をコートすればよい。上記の通り、懸濁液は溶剤中に溶解した結合剤を任意成分として含んでいてもよい。

【００７４】

９．実施例

以下の実施例は例示にすぎず、本発明の技術的範囲を限定するものではない。

【００７５】

実施例１

３種類の蛍光体からなる３種のブレンドを上記の方法で調製した。ブレンドの組成は、各ブレンドと共に用いられる放射源のピーク発光波長に応じて変化させた。一般に、３７０～４０５ｎｍの範囲内にピーク発光波長又は励起波長を有するＬＥＤ放射源については、励起波長が長いほどブレンド中の第１の橙色発光蛍光体の量を増やし、第２の青緑色発光蛍光体及び第３の青色発光蛍光体の量は減らした。励起波長、ブレンドの組成、並びにブレンドのＣＩＥ色座標（ｃｃｘ及びｃｃｙ）、色温度、ＣＲＩ及び視感度を下記の表ＩＩにまとめて示す。

【００７６】

【表２】

表II

励起λ	蛍光体ブレンド (WT %)	ccx	ccy	色温度 (K)	CRI	視感度 (lm/W)
380 mm	SrP (57.5) BASI (21.5) SECA (21.0)	.4011	.3807	3507	70.5	346.4
390 mm	SrP (61.4) BASI (19.4) SECA (19.2)	.3995	.3830	3565	70.7	347.3
405 mm	SrP (73.7) BASI (12.1) SECA (14.2)	.3899	.3791	3767	72.3	349.6

【００７７】

上記表では、以下の略語を使用した。ＢＡＳＩ＝$(Ba_{0.65}, Sr_{0.2}, Ca_{0.1}, Eu_{0.05})_2SiO_4$、ＳＥＣＡ＝$(Sr, Ba, Ca)_5(PO_4)_3Cl:Eu^{2+}$、ＳｒＰ＝$Sr_2P_2O_7:Eu^{2+}, Mn^{2+}$。視感度は、装置の光度と６８３ｌｍ／Ｗとの積として定義される。ここで、６８３ｌｍ／Ｗは５５５ｎｍでのピーク光度である。装置の光度は、$(\int F(\lambda)Y(\lambda)d\lambda)/(\int F(\lambda)d\lambda)$（式中、$F(\lambda)$は発光スペクトルであり、$Y(\lambda)$は目の感度曲線である）として定義される。表ＩＩに例示される通り、ブレンドの色温度は３５０７Ｋから３７６７Ｋまで変化し、ＣＲＩは７０．５から７２．３まで変化し、視感度は３４６．４ｌｍ／Ｗから３４９．６ｌｍ／Ｗまで変化した。これらの高視感度ブレンドは、北米の照明市場で販売される白色光照

明装置用として好ましい。

【００７８】

実施例２

４種類の蛍光体からなる３種のブレンドを上記の方法で調製した。ブレンドの組成は、各ブレンドと共に用いられる放射源のピーク発光波長に応じて変化させた。一般に、３７０～４０５ｎｍの範囲内にピーク発光波長又は励起波長を有するＬＥＤ放射源については、励起波長が長いほどブレンド中の第１、第２及び第３の蛍光体の量を増やし、第４の蛍光体の量は減らした。励起波長、ブレンドの組成、並びにブレンドのＣＩＥ色座標（ｃｃｘ及びｃｃｙ）、色温度、ＣＲＩ及び視感度を下記の表ＩＩＩにまとめて示す。

【００７９】

【表３】

表 III

励起λ	蛍光体ブレンド (WT %)	ccx	ccy	色温度 (K)	CRI	視感度 (lm/W)
380 mm	SrP (12.7) BASI (10.0) SECA (7.4) MgF (69.9)	.4017	.3835	3519	93	285
390 mm	SrP (17.6) BASI (11.8) SECA (9.0) MgF (61.6)	.4065	.3793	3374	93.5	272.2
405 mm	SrP (41.5) BASI (14.2) SECA (12.8) MgF (31.5)	.3967	.3743	3557	91.3	264.7

【００８０】

上記表では、以下の略語を使用した。ＢＡＳＩ＝$(Ba_{0.65}, Sr_{0.2}, Ca_{0.1}, Eu_{0.05})_2SiO_4$、ＳＥＣＡ＝$(Sr, Ba, Ca)_5(PO_4)_3Cl:Eu^{2+}$、ＳｒＰ＝$Sr_2P_2O_7:Eu^{2+}, Mn^{2+}$、及びＭｇＦ＝$3.5MgO*0.5MgF_2*GeO_2:Mn^{4+}$。表ＩＩＩに例示される通り、ブレンドの色温度は３３７４Ｋから３５５７Ｋまで変化し、ＣＲＩは９１．３から９３．５まで変化し、視感度は２６４．７ｌｍ／Ｗから２８５ｌｍ／Ｗまで変化した。表ＩＩＩから、第４の赤色発光蛍光体の添加がＣＲＩの顕著な増大をもたらすことは明らかである。これらの高ＣＲＩブレンドは、ヨーロッパの照明市場で販売される白色光照明装置用として好ましい。

【００８１】

以上、例示を目的として好ましい実施形態について説明してきた。しかし、以上の説明は本発明の技術的範囲を限定するものではなく、本発明の要旨及び技術的範囲内での様々な変更、適用及び置換は当業者には自明であろう。

【図面の簡単な説明】

【図１】

ＣＩＥ色度図を示すグラフである。

【図２】

本発明の一実施形態に係る白色光照明装置の略図である。

【図３】

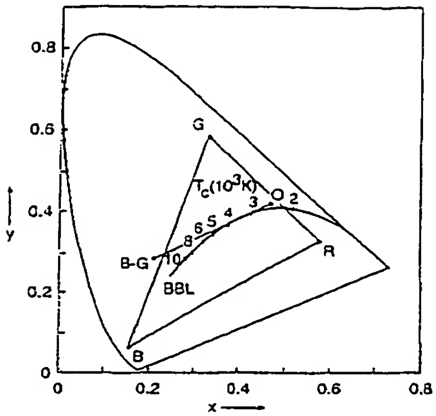
本発明の第１の好ましい実施形態に係るＬＥＤを用いた照明装置の概略断面図である。

【図４】

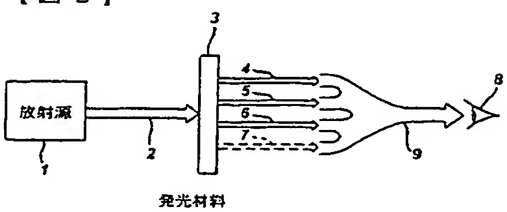
本発明の第１の好ましい実施形態に係るＬＥＤを用いた照明装置の概略断面図である。

【図５】
本発明の第１の好ましい実施形態に係るＬＥＤを用いた照明装置の概略断面図である。
【図６】
本発明の第２の好ましい実施形態に係る蛍光ランプを用いた照明装置の概略断面図である。
【図７】
本発明の第３の好ましい実施形態に係るプラズマディスプレイを用いた照明装置の概略断面図である。
【符号の説明】
１　放射源
２　放射
３　蛍光体
４　橙色光
５　青緑色光
６　青色光
７　赤色光
８　観察者
９　白色光
１１　発光ダイオードチップ
１３　リード線
１５　リードフレーム
１７　シェル
１９　封入材料
２１　発光材料
２３　白色光
２５　放射
３１　蛍光ランプ
３３　ランプカバー
３５　蛍光体被膜
３７　ランプ口金
３９　陰極
４１　交通信号機
４２　第１のガラス板
４３　第２のガラス板
４４　陰極
４５　陽極
４６　蛍光体層
４７　バリヤーリブ
４８　貴ガス空間

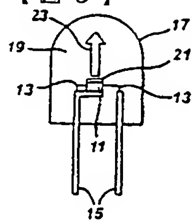
【図１】



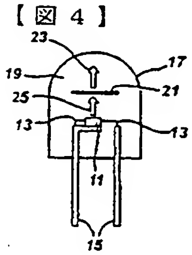
【図２】



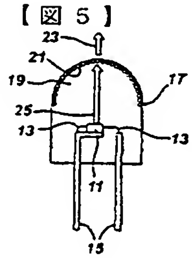
【図３】



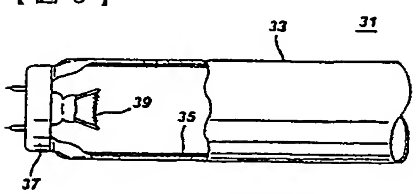
【図４】



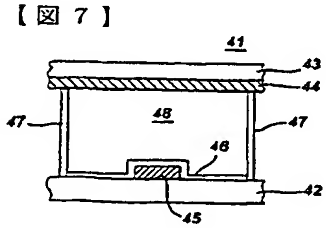
【図５】



【図６】



【図７】



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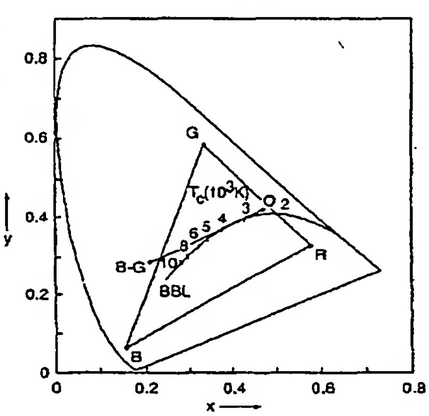
[Continued on next page]

(54) Title: WHITE LIGHT EMITTING PHOSPHOR BLENDS FOR LED DEVICES



(57) Abstract: There is provided a blue-green illumination system, comprising a light emitting diode (11), and at least one luminescent material (21) having at least two peak emission wavelengths, wherein the emission CIE color coordinates of the at least two peak emission wavelengths are located within an area of a pentagon on a CIE chromaticity diagram, whose corners have the following CIE color coordinates: a) x=0.0137 and y=0.4831; b) x=0.2240 and y=0.3890; c) x=0.2800 and y=0.4500; d) x=0.2879 and y=0.5196; and e) x=0.0108 and y=0.7220. The illumination system (51) may be used as the green light of a traffic signal (41). The luminescent material may be a blend of $(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$ ("BAM") and $(Ba_{1-x}Eu_x)(Mg_{2-y}Mn_y)Al_{16}O_{27}$ ("BAMMn") phosphors, where $0 < x \le 0.2$ and $0 < y \le 0.5$.

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WHITE LIGHT EMITTING PHOSPHOR BLENDS FOR LED DEVICES

BACKGROUND OF THE INVENTION

This invention relates generally to a white light illumination system, and specifically to a ceramic phosphor blend for converting UV radiation emitted by a light emitting diode ("LED") to white light.

White light emitting LEDs are used as a backlight in liquid crystal displays and as a replacement for small conventional lamps and fluorescent lamps. As discussed in chapter 10.4 of "The Blue Laser Diode" by S. Nakamura et al., pages 216-221 (Springer 1997), incorporated herein by reference, white light LEDs are fabricated by forming a ceramic phosphor layer on the output surface of a blue light emitting semiconductor LED. Conventionally, the blue LED is an InGaN single quantum well LED and the phosphor is a cerium doped yttrium aluminum garnet ("YAG:Ce"), $Y_3Al_5O_{12}:Ce^{3+}$. The blue light emitted by the LED excites the phosphor, causing it to emit yellow light. The blue light emitted by the LED is transmitted through the phosphor and is mixed with the yellow light emitted by the phosphor. The viewer perceives the mixture of blue and yellow light as white light.

However the blue LED - YAG:Ce phosphor white light illumination system suffers from the following disadvantages. The prior art blue LED - YAG:Ce phosphor system produces white light with a high color temperature ranging from 6000K to 8000K, which is comparable to sunlight, and a typical color rendering index (CRI) of about 70 to 75. In other words, the chromaticity or color coordinates of this system are located adjacent to the Black Body Locus ("BBL") between the color temperatures of 6000K and 8000K on the CIE chromaticity diagram illustrated in Figure 1. The color

temperature of this system can be reduced by increasing the phosphor thickness. However, the increased phosphor thickness decreases the system efficiency.

While the blue LED - YAG:Ce phosphor illumination system with a relatively high color temperature and a relatively low CRI is acceptable to customers in the far east lighting markets, the customers in the North American markets generally prefer an illumination system with a lower color temperature, while the customers European markets generally prefer an illumination system with a high CRI. For example, North American customers generally prefer systems with color temperatures between 3000K and 4100K, while European customers generally prefer systems with a CRI above 90.

The chromaticity coordinates and the CIE chromaticity diagram illustrated in Figure 1 are explained in detail in several text books, such as pages 98-107 of K. H. Butler, "Fluorescent Lamp Phosphors" (The Pennsylvania State University Press 1980) and pages 109-110 of G. Blasse et al., "Luminescent Materials" (Springer-Verlag 1994), both incorporated herein by reference. The chromaticity coordinates (i.e., color points) that lie along the BBL obey Planck's equation: $E(\lambda)=A\lambda^{-5} / (e^{(B/T)} - 1)$, where E is the emission intensity, λ is the emission wavelength, T the color temperature of the black body and A and B are constants. Color coordinates that lie on or near the BBL yield pleasing white light to a human observer. CRI is a relative measurement of how the color rendition of an illumination system compares to that of a black body radiator. The CRI equals 100 if the color coordinates of a set of test colors being illuminated by the illumination system are the same as the coordinates of the same test colors being irradiated by the black body radiator.

Another disadvantage of the blue LED - YAG:Ce phosphor system is that the LED color output (e.g., spectral power distribution and peak emission wavelength) varies with the band gap width of the LED active layer and with the power applied to the LED. During production, a certain percentage of LEDs are manufactured with active layers whose actual band gap width is larger or smaller than the desired width. Thus, the color output of such LEDs deviates from the desired parameters. Furthermore, even if the band gap of a particular LED has the desired width, during LED operation the power applied to the LED frequently deviates from the desired value. This also causes the LED color output to deviate from the desired parameters. Since the light emitted by the system contains a blue component from the LED, if the color output of the LED deviates from the desired parameters, then the light output by the system deviates form the desired parameters as well. A significant deviation from the desired parameters may cause the color output of the system to appear non-white (i.e., bluish or yellowish).

Furthermore, the color output of the blue LED - YAG:Ce phosphor system varies greatly due to frequent, unavoidable, routine deviations from desired parameters (i.e., manufacturing systematic variations) during the production of the LED lamp because the color output of this system is very sensitive to the thickness of the phosphor. If the phosphor is too thin, then more than a desired amount of the blue light emitted by the LED will penetrate through the phosphor, and the combined LED - phosphor system light output will appear bluish, because it is dominated by the output of the blue LED. In contrast, if the phosphor is too thick, then less than a desired amount of the blue LED light will penetrate through the thick YAG:Ce phosphor layer. The combined LED - phosphor system will then appear yellowish, because it is dominated by the yellow output of the YAG:Ce phosphor.

Therefore, the thickness of the phosphor is a critical variable affecting the color output of the prior art system. Unfortunately, it is difficult to control the precise thickness of the phosphor during large scale production of the blue LED - YAG:Ce phosphor system. Variations in phosphor thickness often result in the system output being unsuitable for white light illumination applications, causing the color output of the system to appear non-white (i.e., bluish or yellowish), which leads to an unacceptably low blue LED - YAG:Ce phosphor system manufacturing yield.

The blue LED - YAG:Ce phosphor system also suffers from the halo effect due to the separation of blue and yellow light. The LED emits blue light in a directional fashion. However, the phosphor emits yellow light isotropically (i.e., in all directions). Therefore, when the light output by the system is viewed straight on (i.e., directly at the LED emission), the light appears bluish-white. In contrast, when the light output is viewed at an angle, the light appears yellowish due to the predominance of the yellow phosphor emission. When the light output by such a system is directed onto a flat surface, it appears as a yellowish halo surrounding a bluish area. The present invention is directed to overcoming or at least reducing the problems set forth above.

BRIEF SUMMARY OF THE INVENTION

In accordance with one aspect of the present invention, there is provided a white light illumination system comprising a light emitting diode, a first luminescent material having a peak emission wavelength of about 575 to about 620 nm, a second luminescent material having a peak emission wavelength of about 495 to about 550 nm, which is different from the first luminescent material, and a third luminescent material having a peak

emission wavelength of about 420 to about 480 nm, which is different from the first and second luminescent materials.

In accordance with another aspect of the present invention, there is provided a white light emitting phosphor blend comprising at least three phosphors, wherein the white light emitted by the phosphor blend in response to incident radiation having a peak wavelength between 360 and 420 nm comprises a color temperature between 3000K and 6500K, a CRI above 70 and an efficacy above 200 lm/W.

In accordance with another aspect of the present invention, there is provided a white light illumination system, comprising:

a radiation source;

a first $APO:Eu^{2+},Mn^{2+}$ phosphor, where A comprises at least one of Sr, Ca, Ba or Mg;

a second phosphor selected from at least one of:

a) an $ASiO:Eu^{2+}$ phosphor, where A comprises at least one of Ba, Ca, Sr or Mg;

b) an $ADSiO:Eu^{2+}$ phosphor, where A comprises at least one of Ba, Ca or Sr and D comprises at least one of Mg or Zn; or

c) an $AAlO:Eu^{2+}$ phosphor, where A comprises at least one of Ba, Sr or Ca; and

a third phosphor selected from at least one of:

d) an $AMgAlO:Eu^{2+}$ phosphor where A comprises at least one of Ba, Ca or Sr;

e) a $DPOCl:Eu^{2+}$ phosphor where D comprises at least one of Sr, Ba, Ca or Mg;

f) an $EO*AlO:Eu^{2+}$ phosphor, where E comprises at least one of Ba, Sr or Ca;

g) an EAlO:Eu^{2+} phosphor, where E comprises at least one of Ba, Sr or Ca; or

h) GAlO:Eu^{2+} phosphor, where G comprises at least one of K, Li, Na or Rb.

In accordance with another aspect of the present invention, there is provided a method of making a white light illumination system, comprising blending a first phosphor powder having a peak emission wavelength of about 575 to about 620 nm, a second phosphor powder having a peak emission wavelength of about 495 to about 550 nm, and a third phosphor powder having a peak emission wavelength of about 420 to about 480 nm to form a phosphor powder mixture, and placing the phosphor powder mixture into the white light illumination system adjacent a light emitting diode.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an illustration of a CIE chromaticity diagram.

Figure 2 is schematic illustration of a white light illumination system according to one embodiment of the present invention.

Figures 3-5 are cross-sectional schematic views of illumination systems using an LED according to the first preferred embodiment of the present invention.

Figure 6 is a cross-sectional schematic view of an illumination system using a fluorescent lamp according to the second preferred embodiment of the present invention.

Figure 7 is a cross-sectional schematic view of an illumination system using a plasma display according to the third preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In view of the problems in the prior art, it is desirable to obtain a white light illumination system whose color output is less sensitive to variations during system operation and manufacturing process, such as due to variations in the LED power, the width of the LED active layer band gap and the thickness of the luminescent material. The present inventors have discovered that a color output of the radiation source - luminescent material system is less sensitive to these variations if the color output of the system does not include significant visible radiation emitted by the radiation source, such as an LED. In this case, the color output of the system does not vary significantly with the LED power, band gap width and the luminescent material thickness. The term luminescent material preferably comprises a phosphor in loose or packed powder form.

The color output of the system does not vary significantly with the thickness of the luminescent material if the white light emitted by the system lacks any significant visible component emitted by the radiation source, such as the LED. Therefore, the amount of transmission of the LED radiation through the luminescent material, such as a phosphor, does not affect the color output of the system. This can be achieved in at least two ways.

One way to avoid affecting the color output of the system is by using a radiation source that emits radiation in a wavelength that is not visible to the human eye. For example, an LED may be constructed to emit ultraviolet (UV)

radiation having a wavelength of 380 nm or less that is not visible to the human eye. Furthermore, the human eye is not very sensitive to UV radiation having a wavelength between 380 and 400 nm and to violet light having a wavelength between 400 and 420 nm. Therefore, the radiation emitted by the LED having a wavelength of 420 nm or less would not substantially affect the color output of the LED - phosphor system irrespective of whether the emitted LED radiation is transmitted through the phosphor or not, because radiation having a wavelength of about 420 nm or less is not significantly visible to a human eye.

The second way to avoid affecting the color output of the system is by using a thick luminescent material which does not allow the radiation from the radiation source to pass through it. For example, if the LED emits visible light between 420 and 650 nm, then in order to ensure that the phosphor thickness does not affect the color output of the system, the phosphor should be thick enough to prevent any significant amount of visible light emitted by the LED from penetrating through the phosphor. However, while this way to avoid affecting the color output of the system is possible, it is not preferred because it lowers the output efficiency of the system.

In both cases described above, the color of the visible light emitted by the system is solely dependent on the type of luminescent material used. Therefore, in order for the LED - phosphor system to emit white light, the phosphor should emit white light when it is irradiated by the LED radiation.

Furthermore, by utilizing more than one phosphor the color properties of the white light may be varied to meet the desired color parameters. For example, by selecting certain phosphors in a certain ratio, the color temperature and the CRI of the white light or the efficacy of the system may be optimized. For example, phosphor ratios may be selected to obtain a white

light illumination system with a color temperature of 3000K to 6500K, a CRI of above 70 and an efficacy of above 300 lm/W, which is desirable in the North American markets. A color temperature of 4000 to 6500K is particularly desirable for a flashlight. Alternatively, other phosphor ratios may be selected to obtain a white light illumination system with a color temperature of 3000K to 4100K, a CRI of above 90 and an efficacy of above 200 lm/W, which is desirable in the European markets.

The present inventors have discovered that a when a first orange emitting phosphor having a peak emission wavelength between about 575 and 620 nm, a second blue-green emitting phosphor having a peak emission wavelength between about 495 to about 550 nm, and a third blue emitting phosphor having a peak emission wavelength of about 420 to about 480 are used together, a human observer perceives their combined emission as white light. Furthermore, in order to increase the CRI of the illumination system, a fourth red emitting phosphor having a peak emission wavelength of about 620 nm to about 670 nm may be optionally added.

Figure 2 schematically illustrates the above principle. In Figure 2, a radiation source 1, such as an LED, emits radiation 2 incident on three luminescent materials layers 3, such as the above described first, second and third phosphors. The radiation 2 may have a wavelength to which the human eye is not sensitive, such as 420 nm and below. Alternatively, the phosphors 3 may be too thick to allow significant radiation 2 to penetrate to the other side. After absorbing the incident radiation 2, the first phosphor emits orange light 4 having a peak emission wavelength between 575 and 620 nm, the second phosphor emits blue-green light 5 having a peak emission wavelength between 495 and 550 nm, and the third phosphor emits blue light 6 having a peak emission wavelength between 420 and 480. If present, the fourth

phosphor emits red light 7 having a peak emission wavelength between 620 nm and 670 nm. The human observer 8 perceives the combination of the orange 4, blue-green 5, blue 6 and optionally red 7 light as white light 9. Figure 2 schematically illustrates that different color light 4, 5, 6, 7 emanates from discrete phosphor areas to illustrate the concept of color mixing. However, it should be understood that light 4, 5, 6 and 7 may be emitted from the same area and/or from the entire phosphor if the individual phosphors are blended together to form a single blended phosphor layer 3.

Any luminescent materials, such as phosphors and scintillators may be used in combination with a radiation source to form the white light illumination system. Preferably, the luminescent materials have a high quantum efficiency at a particular emission wavelength of the radiation source. Furthermore, each luminescent material is preferably transparent to the visible light wavelengths emitted by the other luminescent material.

I. <u>The Radiation Source</u>

The radiation source 1 may comprise any radiation source capable of causing an emission from the phosphors. Preferably, the radiation source 1 comprises an LED. However, the radiation source 1 may also comprise a gas, such as mercury in a fluorescent lamp or high pressure mercury vapor lamp, or a noble gas, such as Ne, Ar and/or Xe in a plasma display.

For example, the radiation source 1 may comprise any LED which causes the phosphors 3 to emit radiation 9 which appears white to the human observer 8 when the radiation 2 emitted by the LED is directed onto the phosphors. Thus, the LED may comprise a semiconductor diode based on any suitable III-V, II-VI or IV-IV semiconductor layers and having an emission wavelength of 360 to 420 nm. For example, the LED may contain at least one

semiconductor layer based on GaN, ZnSe or SiC semiconductors. The LED may also contain one or more quantum wells in the active region, if desired. Preferably, the LED active region may comprise a p-n junction comprising GaN, AlGaN and/or InGaN semiconductor layers. The p-n junction may be separated by a thin undoped InGaN layer or by one or more InGaN quantum wells. The LED may have an emission wavelength between 360 and 420 nm, preferably between 370 and 405 nm, most preferably between 370 and 390 nm. However, an LED with an emission wavelength above 420 nm may be used with a thick phosphor, whose thickness prevents the light emitted from the LED from penetrating through the phosphor. For example the LED may have the following wavelengths: 370, 375, 380, 390 or 405 nm.

The radiation source 1 of the white light illumination system has been described above as a semiconductor light emitting diode. However, the radiation source of the present invention is not limited to a semiconductor light emitting diode. For example, the radiation source may comprise a laser diode or an organic light emitting diode (OLED). The preferred white light illumination system described above contains a single radiation source 1. However, if desired, plural radiation sources may be used in the system in order to improve the emitted white light or to combine the emitted white light with a light of a different color(s). For example, the white light emitting system may be used in combination with red, green and/or blue light emitting diodes in a display device.

2. <u>The First Phosphor</u>

The first luminescent material may be any phosphor, which in response to the incident radiation 2 from the radiation source 1, emits visible light having a peak emission wavelength of about 575 to about 620 nm. If the radiation source 1 comprises an LED having a peak emission wavelength

between 360 and 420 nm, then the first phosphor may comprise any commercially available phosphor having the peak emission wavelength between 575 and 620 nm and a high relatively efficacy and quantum efficiency for incident radiation having a peak wavelength between 360 and 420 nm.

Preferably, the first phosphor comprises $APO:Eu^{2+},Mn^{2+}$, where A comprises at least one of Sr, Ca, Ba or Mg. Most preferably, the first phosphor comprises a europium and manganese doped alkaline earth pyrophosphate phosphor, $A_2P_2O_7:Eu^{2+},Mn^{2+}$. The phosphor may be written as $(A_{1-x-y}Eu_xMn_y)_2\,P_2\,O_7$, where $0 < x \leq 0.2$ and $0 < y \leq 0.2$. Preferably, A comprises strontium ions. This phosphor is preferred for an LED radiation source because it has a high efficacy and high quantum efficiency for incident radiation having a peak wavelength between 360 and 420 nm, such as that emitted by an LED. Alternatively, the first phosphor may comprise $A_2P_2O_8:Eu^{2+},Mn^{2+}$, where A comprises at least one of Sr, Ca, Ba or Mg.

In the Eu^{2+} and Mn^{2+} doped alkaline earth pyrophosphate phosphor, the Eu ions generally act as sensitizers and Mn ions generally act as activators. Thus, the Eu ions absorb the incident energy (i.e., photons) emitted by the radiation source and transfer the absorbed energy to the Mn ions. The Mn ions are promoted to an excited state by the absorbed transferred energy and emit a broad radiation band having a peak wavelength that varies from about 575 to 595 nm when the A ions comprise Sr ions. Alternatively, A may comprise 50 molar percent Sr ions and 50 molar percent Mg ions, such that the $APO:Eu^{2+},Mn^{2+}$ phosphor comprises a $SrMgP_2O_7:Eu^{2+},Mn^{2+}$ phosphor which has a peak wavelength of about 615 nm.

3. The Second Phosphor

The second luminescent material may be any phosphor, which in response to the incident radiation 2 from the radiation source 1, emits visible light having a peak emission wavelength of about 495 nm to about 550 nm. If the radiation source 1 comprises an LED having a peak emission wavelength between 360 and 420 nm, then the second phosphor may comprise any commercially available phosphor having the peak emission wavelength between 495 and 550 nm and a high relatively efficacy and quantum efficiency for incident radiation having a peak wavelength between 360 and 420 nm. For example, the following three Eu^{2+} activated alkaline earth silicate and alkaline earth aluminate phosphors fit this criteria.

One such phosphor is a divalent europium activated alkaline earth silicate phosphor, $ASiO:Eu^{2+}$, where A comprises at least one of Ba, Ca, Sr or Mg. Preferably, the $ASiO:Eu^{2+}$ phosphor has the following composition: $A_2SiO_4:Eu^{2+}$, where A preferably comprises at least 60% Ba, 30% or less Sr and 10% or less Ca. If A comprises Ba or Ca, then the phosphor peak emission wavelength is about 505 nm. If A comprises Sr, then the phosphor peak emission wavelength is about 580 nm. Therefore, A most preferably comprises Ba ions or Ba ions with some Ca and/or Sr ions to obtain a desired peak wavelength.

In the alkaline earth silicate phosphor, the europium activator substitutes on the alkaline earth lattice site, such that the phosphor may be written as: $((Ba,Sr,Ca)_{1-x}Eu_x)_2SiO_4$, where $0 < x \leq 0.2$. The alkaline earth silicate phosphor may also contain other impurities and dopants. For example, the phosphor may contain a small amount of fluorine incorporated during powder processing from a fluorine containing flux compound, such as BaF_2 or EuF_3.

Another divalent europium activated alkaline earth silicate phosphor, ADSiO:Eu^{2+} where A comprises at least one of Ba, Ca or Sr and D comprises at least one of Mg and Zn, is suitable as the second phosphor. Preferably, the ADSiO:Eu^{2+} phosphor has the following composition: $A_2DSi_2O_7$:Eu^{2+}. The peak emission wavelength and the relative quantum efficiency of each isomorphous phosphor is illustrated in Table I below:

Table I

	A	D	A	D	A	D	A	D	A	D	A	D
	Ca	Mg	Sr	Mg	Sr	Zn	Sr/ Ba	Mg	Ba	Mg	Ba	Zn
Peak λ	535		470		470		440		500		505	

Therefore, A most preferably comprises Ba ions and/or Ba ions with some Ca or Sr ions in order to obtain the desired peak wavelength.

In the alkaline earth silicate phosphor, the europium activator substitutes on the alkaline earth lattice site, such that the phosphor may be written as: $(A_{1-x}Eu_x)_2DSi_2O_7$, where $0 < x \leq 0.2$. The alkaline earth silicate phosphor may also contain other impurities and dopants. For example, the phosphor may contain a small amount of fluorine incorporated during powder processing from a fluorine containing flux compound, such as BaF_2 or EuF_3.

A divalent europium activated alkaline earth aluminate phosphor, AAlO:Eu^{2+}, where A comprises at least one of Ba, Sr or Ca is also suitable for use as the second phosphor. Preferably, the AAlO:Eu^{2+} phosphor has the following composition: AAl_2O_4:Eu^{2+}, where A comprises at least 50% Sr, preferably at least 80% Sr and 20% or less Ba. If A comprises Ba, then the phosphor peak emission wavelength is about 505 nm. If A comprises Sr, then

the phosphor peak emission wavelength is about 520 nm. If A comprises Ca, then the phosphor peak emission wavelength is about 440 nm. Therefore, A most preferably comprises Sr or Sr and Ba ions in order to obtain the desired peak wavelength.

In the alkaline earth aluminate phosphor, the europium activator substitutes on the alkaline earth lattice site, such that the phosphor may be written as: $(A_{1-x}Eu_x)Al_2O_4$, where $0 < x \leq 0.2$. The alkaline earth aluminate phosphor may also contain other impurities and dopants, such as fluorine incorporated from a flux.

The europium activated alkaline earth silicate phosphors are described in detail in G. Blasse et al., *"Fluorescence of Eu^{2+} Activated Silicates"* 23 Philips Res. Repts. 189-200 (1968), incorporated herein by reference. The europium activated alkaline earth aluminates phosphors are described in detail in G. Blasse et al., *"Fluorescence of Eu^{2+} Activated Alkaline-Earth Aluminates"* 23 Philips Res. Repts. 201-206 (1968), incorporated herein by reference. These references also illustrate the emission and excitation spectra of the above described phosphors.

In one aspect of the present invention, the second phosphor may comprise a plurality of the silicate and aluminate phosphors in order to optimize the color or other emission properties, if desired. For example, the second phosphor may comprise the following combinations: $ASiO:Eu^{2+}$ and $ADSiO:Eu^{2+}$, $ASiO:Eu^{2+}$ and $AAlO:Eu^{2+}$, $ADSiO:Eu^{2+}$ and $AAlO:Eu^{2+}$, $ASiO:Eu^{2+}$ and $ADSiO:Eu^{2+}$ and $AAlO:Eu^{2+}$. The above mentioned phosphors may be placed into the same illumination system as overlying layers or as a blend.

4. <u>The Third Phosphor</u>

The third luminescent material may be any phosphor, which in response to the incident radiation 2 from the radiation source 1, emits visible light having a peak emission wavelength of about 420 nm to about 480 nm. If the radiation source 1 comprises an LED having a peak emission wavelength between 360 and 420 nm, then the third phosphor may comprise any commercially available phosphor having the peak emission wavelength between 420 and 480 nm and a high efficacy and quantum efficiency for incident radiation having a peak wavelength between 360 and 420 nm. For example, the following two commercially available Eu^{2+} activated phosphors fit this criteria.

One example of a third phosphor having a peak emission wavelength between 420 and 480 nm is the divalent europium activated halophosphate phosphor, $DPO_4Cl:Eu^{2+}$, where D comprises at least one of Sr, Ba, Ca or Mg. The $DPO_4Cl:Eu^{2+}$ phosphor preferably comprises the commercially available "SECA" phosphor, $D_5(PO_4)_3Cl:Eu^{2+}$. A small amount of phosphate may be replaced by a small amount of borate to increase the emission intensity. The peak emission wavelength of this phosphor varies with the ratio of strontium to other alkaline earth ions. When D comprises only Sr ions, the peak emission wavelength is 447 nm. Substitution of the Sr ions with Ba ions cause the peak emission to shift to a lower wavelength, while substitution of the Sr ions with Ca ions cause the peak emission to shift to a higher wavelength. For example, if the 0.5 moles out of the 5 moles of Sr ions are substituted with 0.5 moles of Ca ions, then the peak emission shifts to 452 nm. If 1 mole of Sr ions are substituted with 0.5 moles of Ca ions and 0.5 moles of Ba ions, then the peak emission shifts to 445 nm. Therefore, the preferred SECA phosphor composition is $(Sr_{1-y-z}Ba_yCa_z)_{5-x}Eu_x(PO_4)_3Cl$, where $0.01 \leq x \leq 0.2$, $0 \leq y \leq 0.1$ and $0 \leq z \leq 0.1$ and the preferred peak emission wavelength is 447-450 nm.

Another example of a third phosphor having a peak emission wavelength between 420 and 480 nm is the divalent europium activated alkaline earth metal aluminate phosphor, $AMgAlO:Eu^{2+}$, where A comprises at least one of Ba, Ca or Sr. The preferred aluminate phosphor may have various magnesium, aluminum and oxygen molar ratios and is commercially available under the name "BAM." For example, one preferred BAM phosphor may be written as $AMg_2Al_{16}O_{27}:Eu^{2+}$, where A preferably comprises at least 90% Ba ions. This phosphor has the following formula: $(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$, where $0 < x \leq 0.2$, preferably x=0.07. Alternatively, BAM has the following molar ratios: $BaMgAl_{10}O_{17}$: Eu^{2+}. The BAM phosphor has an emission peak at about 450 nm due to the Eu^{2+} activator on the A lattice site. The emission peak shifts from 450 nm to a higher wavelength as the amount of barium ions substituted with strontium ions increases.

Other examples of a third phosphor having a peak emission wavelength between 420 and 480 nm comprise divalent europium activated aluminate phosphors selected from an $EO^*AlO:Eu^{2+}$ phosphor, an $EAlO:Eu^{2+}$ phosphor and/or a $GAlO:Eu^{2+}$ phosphor, where E comprises at least one of Ba, Sr or Ca ions and G comprises at least one of K, Li, Na or Rb ions. Preferably, E comprises Ba ions substituted with 0-10% of Sr or Ca ions and G comprises K substituted with 0-10% of Li, Na or Rb ions. Preferably, the $EO^*AlO:Eu^{2+}$ phosphor comprises $z(BaO)^*6Al_2O_3:Eu^{2+}$ or $z(Ba_{1-x}Eu_x)O^*6Al_2O_3$, where $1 \leq z \leq 1.8$, and $0 < x \leq 0.2$. The $EAlO:Eu^{2+}$ phosphor preferably comprises $BaAl_{12}O_{19}:Eu^{2+}$ or $(Ba_{1-x}Eu_x)Al_{12}O_{19}$ where $0 < x \leq 0.2$. The $GAlO:Eu^{2+}$ phosphor preferably comprises $KAl_{11}O_{17.07}:Eu^{2+}$ or $(K_{1-x}Eu_x)Al_{11}O_{17.07}$, where $0 < x \leq 0.2$. The EO*AlO, EAlO and GAlO phosphors are described in the following references, each incorporated herein by reference in their entirety: A.L.N. Stevels and A.D.M. Schrama-de Pauw, Journal of the Electrochemical Society, 123 (1976) 691; J.M.P.J. Verstegen, Journal of the

Electrochemical Society, 121 (1974) 1623; and C.R. Ronda and B.M.J. Smets, Journal of the Electrochemical Society, 136 (1989) 570.

In one aspect of the present invention, the third phosphor may comprise a blend of SECA, BAM and/or one or more aluminate phosphors in order to optimize the color or other emission properties, if desired.

5. <u>The Optional Fourth Phosphor</u>

The optional fourth luminescent material may be any phosphor, which in response to the incident radiation 2 from the radiation source 1, emits visible light having a peak emission wavelength of about 620 nm to about 670 nm. This red emitting phosphor may be added to the first, second and third phosphors to improve the CRI of the white light emitted by the combination of phosphors. Since the CRI is a measure of how the test colors appear under illumination from the phosphor compared to under illumination from a black body, the white light emitted from phosphor will better approximate the white light from a black body if the phosphor emission comprises additional individual colors. If the radiation source 1 comprises an LED having a peak emission wavelength between 360 and 420 nm, then the second phosphor may comprise any commercially available phosphor having the peak emission wavelength between 620 and 670 nm and a high efficacy and quantum efficiency for incident radiation having a peak wavelength between 360 and 420 nm. For example, the Mn^{4+} activated fluorogermanate phosphor fits this criteria.

For example, the fluorogermanate phosphor may comprise a magnesium fluorogermanate phosphor, $MgO{*}MgF{*}GeO:Mn^{4+}$, preferably the commercially available $3.5MgO{*}0.5MgF_2{*}GeO_2:Mn^{4+}$ phosphor. This

phosphor emits a structured red luminescence band having six peaks at room temperature between 623 and 664 nm.

6. The Phosphor Blend

According to one preferred aspect of the present invention, the first, second, third and optionally fourth phosphors are interspersed. Most preferably, the phosphors are blended together to form a uniform blend. The amount of each phosphor in the blend depends on the type of phosphor and the type of radiation source used. However, the first, second, third and optionally fourth phosphors should be blended such that the combination of the emission 9 from the phosphors appears white to a human observer 8.

Alternatively, the first, second, third and optionally fourth phosphors may comprise discrete layers formed over the radiation source 1. However, the upper phosphor layers should be substantially transparent to the radiation emitted by the lower phosphors.

The composition of the phosphor powder blend may be optimized based on the number of phosphors used, the desired blend CRI and efficacy, the composition of the phosphors and the peak emission wavelength of the radiation source 1. For example, in order to decrease the color temperature of the phosphor blend for a constant excitation radiation wavelength, the ratio of blue to orange emitting phosphors may be decreased. In order to increase the CRI of the phosphor blend, a fourth phosphor, such as a red emitting phosphor, may be added to the blend.

The phosphor blend of a first preferred aspect of the present invention preferably contains at least three phosphors, wherein the white light emitted by the phosphor blend in response to incident or excitation radiation having a peak wavelength between 360 and 420 nm comprises a color temperature

between 3000K and 6500K, a CRI above 70 and an efficacy of above 200 lm/W. More preferably, the blend efficacy is above 264 lm/W and the color temperature is between 3300K and 4100K. Most preferably the efficacy is above 340 lm/W.

The preferred first, second and third phosphors of the first preferred aspect of the invention comprise strontium pyrophosphate, alkali earth silicate and SECA, respectively. The composition of the blend of the first preferred aspect comprises about 55 to about 75 weight percent $Sr_2P_2O_7{:}Eu^{2+},Mn^{2+}$ phosphor, about 11 to about 22 weight percent $(Ba,Sr,Ca)_2SiO_4{:}Eu^{2+}$ phosphor and about 13 to about 22 weight percent $(Sr,Ba,Ca,Mg)_5(PO_4)_3Cl{:}Eu^{2+}$ phosphor.

The high CRI phosphor blend according to a second preferred aspect of the present invention preferably contains at least four phosphors, wherein the white light emitted by the phosphor blend in response to incident radiation having a peak wavelength between 360 and 420 nm comprises a color temperature between 3000K and 4100K, a CRI above 90 and an efficacy above 200 lm/W. More preferably, the blend efficacy is above 264 lm/W and the color temperature is between 3300K and 3800K.

The preferred first, second, third and fourth phosphors of the second preferred aspect of the invention comprise strontium pyrophosphate, alkali earth silicate, SECA, and magnesium fluorogermanate, respectively. The composition of the blend of the second preferred aspect comprises about 11 to about 43 weight percent $Sr_2P_2O_7{:}Eu^{2+},Mn^{2+}$ phosphor, about 9 to about 15 weight percent $(Ba,Sr,Ca)_2SiO_4{:}Eu^{2+}$ phosphor, about 6 to about 14 weight percent $(Sr,Ba,Ca,Mg)_5(PO_4)_3Cl{:}Eu^{2+}$ phosphor, and about 30 to about 71 weight percent $3.5MgO{*}0.5MgF_2{*}GeO_2{:}Mn^{4+}$ phosphor.

However, other phosphors having the desired peak emission wavelengths may be used instead of or in addition to the phosphors described above. For example, for radiation sources other than LEDs, phosphors that have a high efficacy and high quantum efficiency for incident radiation having a peak wavelength of 254 nm and 147 nm, may be used for fluorescent lamp and plasma display applications, respectively. The mercury gas emission in a fluorescent lamp has a peak emission wavelength of 254 nm and Xe plasma discharge in a plasma display has a peak emission wavelength of 147 nm.

7. The Illumination System

According to the first preferred embodiment of the present invention, the first, second, third and optionally fourth phosphor powders are placed into a white light illumination system containing an LED radiation source. The white light illumination system may have various different structures.

The first preferred structure is schematically illustrated in Figure 3. The illumination system includes a light emitting diode chip 11 and leads 13 electrically attached to the LED chip. The leads 13 may comprise thin wires supported by a thicker lead frame(s) 15 or the leads may comprise self supported electrodes and the lead frame may be omitted. The leads 13 provide current to the LED chip 11 and thus cause the LED chip 11 to emit radiation.

The LED chip 11 is encapsulated within a shell 17 which encloses the LED chip and an encapsulant material 19. Preferably, the encapsulant comprises a UV resistant epoxy. The shell 17 may be, for example, glass or plastic. The encapsulant material may be, for example, an

epoxy or a polymer material, such as silicone. However, a separate shell 17 may be omitted and the outer surface of the encapsulant material 19 may comprise the shell 17. The LED chip 11 may be supported, for example, by the lead frame 15, by the self supporting electrodes, the bottom of the shell 17 or by a pedestal mounted to the shell or to the lead frame.

The first preferred structure of the illumination system includes a phosphor layer 21 comprising the first, second, third and optionally fourth phosphors. The phosphor layer 21 may be formed over or directly on the light emitting surface of the LED chip 11 by coating and drying a suspension containing the first, second, third and optionally fourth phosphor powders over the LED chip 11. After drying, the phosphor powders form a solid phosphor layer or coating 21. Both the shell 17 and the encapsulant 19 should be transparent to allow white light 23 to be transmitted through those elements. The phosphor emits white light 23 which comprises the orange, blue-green, blue and optionally red light emitted by the first, second, third and optionally fourth phosphors, respectively.

Figure 4 illustrates a second preferred structure of the system according to the first preferred embodiment of the present invention. The structure of Figure 4 is the same as that of Figure 3, except that the phosphor powders are interspersed within the encapsulant material 19, instead of being formed over the LED chip 11. The first phosphor powders may be

interspersed within a single region of the encapsulant material 19 or throughout the entire volume of the encapsulant material. The phosphor powders are interspersed within the encapsulant material, for example, by adding the powders to a polymer precursor, and then curing the polymer precursor to solidify the polymer material. Alternatively, the phosphor powders may be mixed in with the epoxy encapsulant. Other phosphor interspersion methods may also be used. The phosphor powders may be premixed prior to adding a mix of these powders to the encapsulant material 19 or the phosphor powders may be added to the encapsulant material 19 separately. Alternatively, a solid phosphor layer 21 comprising the first, second, third and optionally fourth phosphors may be inserted into the encapsulant material 19 if desired. In this structure, the phosphor layer 21 absorbs the radiation 25 emitted by the LED and in response, emits white light 23.

Figure 5 illustrates a third preferred structure of the system according to the first preferred embodiment of the present invention. The structure of Figure 5 is the same as that of Figure 3, except that the phosphor layer 21 containing the first, second, third and optionally fourth phosphors is formed on the shell 17, instead of being formed over the LED chip 11. The phosphor layer 21 is preferably formed on the inside surface of the shell 17, although the phosphor layer 21 may be formed on the outside surface of the

shell, if desired. The phosphor layer 21 may be coated on the entire surface of the shell or only a top portion of the surface of the shell 17.

Of course, the embodiments of Figures 3-5 may be combined and the phosphor may be located in any two or all three locations or in any other suitable location, such as separately from the shell or integrated into the LED.

According to the second preferred embodiment of the present invention, the first, second, third and optionally fourth powders are placed into a white light illumination system containing a fluorescent lamp radiation source. A portion of a fluorescent lamp is schematically illustrated in Figure 6. The lamp 31 contains a phosphor coating 35 comprising the first, second, third and optionally fourth phosphors on a surface of the lamp cover 33, preferably the inner surface. The fluorescent lamp 31 also preferably contains a lamp base 37 and a cathode 39. The lamp cover 33 encloses a gas, such as mercury, which emits UV radiation in response to a voltage applied to the cathode 39.

According to the third preferred embodiment of the present invention, the first, second, third and optionally fourth phosphor powders are placed into a white light illumination system containing a plasma display device. Any plasma display device, such as an AC or a DC plasma display panel may be used, such as the devices described on pages 623-639 of the *Phosphor Handbook*, Edited by S. Shionoya and W.M. Yen, CRC Press, (1987, 1999), incorporated herein by reference. Figure 7 schematically illustrates one cell of a DC plasma display device 41. The cell contains a first glass plate 42, a second glass plate 43, at least one cathode 44, at least one anode 45, a phosphor layer 46 comprising the first, second, third and optionally fourth phosphors, barrier ribs 47 and a noble gas space 48. In an AC plasma display

device, an extra dielectric layer is added between the cathode and the gas space 48. An application of a voltage between the anode 45 and the cathode 44 causes the noble gas in space 48 to emit short wavelength vacuum ultraviolet radiation (VUV), which excites the phosphor layer 46 causing it to emit white light.

3. The Processing Method

The individual phosphors may be made, for example, by any ceramic powder method, such as a wet chemical method or a solid state method.

Preferably, the method of making the first phosphor comprising europium and manganese doped strontium pyrophosphate phosphor comprises the following steps. First, the starting compounds of the first phosphor material are manually blended or mixed in a crucible or mechanically blended or mixed in another suitable container, such as a ball mill, to form a starting powder mixture. The starting compounds may comprise any oxide, phosphate, hydroxide, oxalate, carbonate and/or nitrate starting phosphor compound. The preferred starting phosphor compounds comprise strontium hydrogen phosphate, $SrHPO_4$, manganese carbonate $MnCO_3$, europium oxide, Eu_2O_3, and ammonium hydrogen phosphate $(NH_4)HPO_4$ powders. The $(NH_4)HPO_4$ powder is preferably added in an amount comprising 2% in excess of the stoichiometric ratio per mole of the first phosphor produced. A small excess of the Sr compound may also be

added if desired. Calcium, barium and magnesium starting compounds may also be added if it is desired to substitute some or all of the strontium with calcium, barium and/or magnesium. The starting powder mixture is then heated in air at about 300 to 800 °C for about 1-5 hours, preferably at 600 °C. The resulting powder is then re-blended and subsequently fired in a reducing atmosphere at about 1000 to 1250 °C, preferably 1000 °C, to form a calcined phosphor body or cake. Preferably the starting powder mixture is calcined in a furnace in an atmosphere comprising nitrogen and 0.1 to 10% hydrogen for four to ten hours, preferably eight hours, and subsequently cooled in the same atmosphere by turning off the furnace.

Preferably, the method of making the second preferred $(Ba,Sr,Ca)_2SiO_4:Eu^{2+}$ phosphor comprises the following steps. First, the starting compounds of the phosphor are manually blended or mixed in a crucible or mechanically blended or mixed in another suitable container, such as a ball mill, to form a starting powder mixture. The starting compounds may comprise any oxide, hydroxide, oxalate, carbonate and/or nitrate starting phosphor compound. The preferred starting phosphor compounds comprise barium carbonate $BaCO_3$, strontium carbonate $SrCO_3$, calcium carbonate $CaCO_3$, europium oxide, Eu_2O_3, and silicic acid, $SiO_2{*}xH_2O$. Preferably, a flux, such as CaF_2 is added to the starting materials in an amount of 0.5 to 3 mole percent per mole of the phosphor produced. The starting

powder mixture is then fired a first time in a carbon containing atmosphere, such as in a charcoal containing atmosphere at 1200 to 1400 °C for 5 to 7 hours to form a first calcined phosphor body or cake. The resultant cake is then ground and milled to a powder. This powder is then annealed or fired a second time in a reducing atmosphere at about 900 to 1200 °C to form a second calcined phosphor body or cake. Preferably the powder is annealed in a furnace in an atmosphere comprising nitrogen and 0.1 to 10% hydrogen for two to six hours.

The solid calcined phosphor bodies may be converted to a first phosphor powder in order to easily coat the phosphor powder on a portion of the white light illumination system. The solid phosphor body may be converted to the first phosphor powder by any crushing, milling or pulverizing method, such as wet milling, dry milling, jet milling or crushing. Preferably, the solid body is wet milled in propanol, methanol and/or water, and subsequently dried.

The third and fourth phosphors are commercially available as phosphor powders and thus, their exact method of manufacture is not significant. The synthesis of BAM and SECA phosphors is described on pages 398-399 and 416-419 of S. Shionoya et al., *Phosphor Handbook*, CRC Press (1987, 1999), incorporated herein by reference. In general, a method of making a commercial BAM phosphor involves blending starting materials comprising barium carbonate, magnesium carbonate, alumina or aluminum hydroxide, europium oxide and optionally a flux, such as aluminum fluoride or barium chloride. The starting powder mixture is then fired in a reducing atmosphere at about 1200 to 1400 °C to form a calcined phosphor body or cake. The cake

may be reground and refired under the same conditions. A method of making a commercial SECA phosphor involves blending starting materials comprising strontium carbonate, strontium orthophosphate, strontium chloride and europium oxide. The starting powder mixture is then fired in a reducing atmosphere at about 1000 to 1200 °C to form a calcined phosphor body or cake. The cake is then ground into a phosphor powder.

The first, second, third and optionally fourth phosphor powders are then blended or mixed together to form a phosphor powder blend or mixture. The powders may be manually blended in a crucible or mechanically blended in another suitable container, such as a ball mill. Of course, the phosphor powder blend may contain more than four powders, if desired. Alternatively, the bodies may be pulverized and blended together.

The phosphor powder blend is then placed into the white light illumination system. For example, the phosphor powder blend may be placed over the LED chip, interspersed into the encapsulant material or coated onto the surface of the shell, as described above with respect to the first preferred embodiment of the present invention.

If the phosphor powder blend is coated onto the LED chip or the shell, then preferably, a suspension of the phosphor powder blend and a liquid is used to coat the LED chip or the shell surface. The suspension may also optionally contain a binder in a solvent. Preferably, the binder comprises an organic material, such as nitrocellulose or ethylcellulose, in a solvent such as butyl acetate or xylol. The binder enhances the adhesion of the powder particles to each other and to the LED or the shell. However, the binder may be omitted to simplify processing, if desired. After coating, the suspension is dried and may be heated to evaporate the binder. The phosphor powder blend acts as the phosphor layer 21 after drying the solvent.

If the phosphor blend is to be interspersed within the encapsulant material 19, then the phosphor blend may be added to a polymer precursor, and then the polymer precursor may be cured to solidify the polymer material. Alternatively, the phosphor blend may be mixed in with the epoxy encapsulant. Other phosphor interspersion methods may also be used.

If the phosphor blend is placed into a fluorescent lamp or a plasma display, then a suspension of the phosphor powder blend and a liquid is used to coat the lamp or plasma display interior surface. The suspension may also optionally contain a binder in a solvent, as described above.

9. Specific Examples

The following examples are merely illustrative; and should not be construed to be any sort of limitation on the scope of the claimed invention.

Example 1

Three blends of three phosphors were prepared by the above mentioned process. The blend composition was varied based on the peak emission wavelength of the radiation source to be used with the blend. In general, for LED radiation sources having a peak emission or excitation wavelength between 370 and 405 nm, the amount of the first orange emitting phosphor in the blend increased while the amount of the second blue-green and third blue emitting phosphors decreased with increasing excitation wavelength. The excitation wavelength, the blend composition, the CIE color coordinates (ccx and ccy), the color temperature, the CRI and the efficacy of the blend are summarized in Table II, below.

Table II

EXCITATION λ	PHOSPHOR BLEND (WT %)	ccx	ccy	Color T (K)	CRI	Efficacy (lm/W)
380 nm	SrP (57.5) BASI (21.5) SECA (21.0)	.4011	.3807	3507	70.5	346.4
390 nm	SrP (61.4) BASI (19.4) SECA (19.2)	.3995	.3830	3565	70.7	347.3
405 nm	SrP (73.7) BASI (12.1) SECA (14.2)	.3899	.3791	3767	72.3	349.6

In the above table, the following abbreviations were used: BASI = $(Ba_{0.65}Sr_{0.2}Ca_{0.1}Eu_{0.05})_2SiO_4$; SECA = $(Sr,Ba,Ca)_5(PO4)_3Cl:Eu^{2+}$; SrP = $Sr_2P_2O_7:Eu^{2+}Mn^{2+}$. Efficacy is defined as the product of the system luminosity times 683 lm/W, where 683 lm/W is the peak luminosity at 555 nm. System luminosity is defined as $(\int F(\lambda)\, Y(\lambda)\, d\lambda) / (\int F(\lambda)\, d\lambda)$, where $F(\lambda)$ is the emission spectrum and $Y(\lambda)$ is the eye sensitivity curve. As illustrated in Table II, the color temperature of the blends varied from 3507 to 3767 K, the CRI varied from 70.5 to 72.3 and the efficacy varied from 346.4 to 349.6 lm/W. These high efficacy blends are preferred for the white light illumination systems sold in the North American lighting market.

Example 2

Three blends of four phosphors were prepared by the above mentioned process. The blend composition was varied based on the peak

emission wavelength of the radiation source to be used with the blend. In general, for LED radiation sources having a peak emission or excitation wavelength between 370 and 405 nm, the amount of the first, second and third phosphors in the blend increased while the amount of the fourth phosphor decreased, with increasing excitation wavelength. The excitation wavelength, the blend composition, the CIE color coordinates (ccx and ccy), the color temperature, the CRI and the efficacy of the blend are summarized in Table III, below.

Table III

EXCITATION λ	PHOSPHOR BLEND (WT %)	ccx	ccy	Color T (K)	CRI	Efficacy (lm/W)
380 nm	SrP (12.7) BASI (10.0) SECA (7.4) MgF (69.9)	.4017	.3835	3519	93	285
390 nm	SrP (17.6) BASI (11.8) SECA (9.0) MgF (61.6)	.4065	.3793	3374	93.5	272.2
405 nm	SrP (41.5) BASI (14.2) SECA (12.8) MgF (31.5)	.3967	.3743	3557	91.3	264.7

In the above table, the following abbreviations were used: BASI = $(Ba_{0.65}Sr_{0.2}Ca_{0.1}Eu_{0.05})_2SiO_4$; SECA = $(Sr,Ba,Ca)_5(PO4)_3Cl:Eu^{2+}$; SrP = $Sr_2P_2O_7:Eu^{2+}Mn^{2+}$ and MgF = $3.5MgO{*}0.5MgF_2{*}GeO_2:Mn^{4+}$. As illustrated in Table III, the color temperature of the blends varied from 3374 to 3557 K, the

CRI varied from 91.3 to 93.5 and the efficacy varied from 264.7 to 285 lm/W. From Table III, it is apparent that the addition of the fourth red emitting phosphor results in a significant CRI increase. These high CRI blends are preferred for the white light illumination systems sold in the European lighting market.

The preferred embodiments have been set forth herein for the purpose of illustration. However, this description should not be deemed to be a limitation on the scope of the invention. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and scope of the claimed inventive concept.

WHAT IS CLAIMED IS:

1. A blue-green illumination system, comprising:
a light emitting diode (11); and
at least one luminescent material (21) having at least two peak emission wavelengths, wherein the emission CIE color coordinates of the at least two peak emission wavelengths are located within an area of a pentagon on a CIE chromaticity diagram, whose corners have the following CIE color coordinates:
e) x=0.0137 and y=0.4831;
b) x=0.2240 and y=0.3890;
c) x=0.2800 and y=0.4500;
g) x=0.2879 and y=0.5196; and
h) x=0.0108 and y=0.7220.

2. The system of claim 1, wherein:
the light emitted by the system lacks any significant visible component emitted by the light emitting diode (11).

3. The system of claim 2, wherein the light emitting diode (11) peak emission wavelength is between 360 and 420 nm; and

4. The system of claim 3, wherein the light emitting diode (11) contains an InGaN active layer having a peak emission wavelength between 370 and 405 nm.

5. The system of claim 4, wherein the luminescent material (21) emission CIE color coordinates are x=0.1 ± 0.05 and y=0.52 ± 0.05.

6. The system of claim 1, wherein the emission CIE color coordinates of the at least one luminescent material are located within an area of a quadrilateral on a CIE chromaticity diagram, whose corners have the following CIE color coordinates:
a) x=0.000 and y=0.506;

b) $x=0.224$ and $y=0.389$;

c) $x=0.280$ and $y=0.450$; and

d) $x=0.000$ and $y=0.730$.

7. The system of claim 1, wherein the emission CIE color coordinates of the at least one luminescent material are located within an area of a quadrilateral on a CIE chromaticity diagram, whose corners have the following CIE color coordinates:

e) $x=0.0137$ and $y=0.4831$;

f) $x=0.2094$ and $y=0.3953$;

g) $x=0.2879$ and $y=0.5196$; and

h) $x=0.0108$ and $y=0.7220$.

8. The system of claim 1, wherein:

the at least one luminescent material (21) comprises a single $AMgAlO:Eu^{2+},Mn^{2+}$ phosphor; and

A comprises at least one of Ba, Ca or Sr.

9. The system of claim 8, wherein:

the $AMgAlO:Eu^{2+},Mn^{2+}$ phosphor comprises an $AMg_2Al_{16}O_{27}:Eu^{2+},Mn^{2+}$ phosphor; and

A comprises at least 90% Ba.

10. The system of claim 9, wherein:

the $AMg_2Al_{16}O_{27}:Eu^{2+}, Mn^{2+}$ phosphor comprises a $Ba_{1-x}Eu_xMg_{2-y}Mn_yAl_{16}O_{27}$ phosphor:

$0 < x \leq 0.2$; and

$0.05 \leq y \leq 0.5$

11. The system of claim 1, wherein:

the at least one luminescent material (21) comprises a single phosphor selected from:

i) an $EO*AlO:Eu^{2+},Mn^{2+}$ phosphor, where E comprises at least one of Ba, Sr or Ca;

ii) an $EAlO:Eu^{2+},Mn^{2+}$ phosphor, where E comprises at least one of Ba, Sr or Ca; or

iii) a $GAlO:Eu^{2+},Mn^{2+}$ phosphor, where G comprises at least one of K, Li, Na or Rb.

12. The system of claim 11, wherein:
the $EO*AlO:Eu^{2+},Mn^{2+}$ phosphor comprises $xBaO*6Al_2O_3:Eu^{2+},Mn^{2+}$;
the $EAlO:Eu^{2+},Mn^{2+}$ phosphor comprises $(Ba_{1-x}Eu_x)Al_{12-y}Mn_yO_{19-0.5y}$;
the $GAlO:Eu^{2+},Mn^{2+}$ phosphor comprises $(K_{1-x}Eu_x)Al_{11-y}Mn_yO_{17-0.5y}$.

13. The system of claim 1, wherein:
the at least one luminescent material (21) comprises a first phosphor having a first peak emission wavelength below 505 nm and a second phosphor having a second peak emission wavelength above 505 nm.

14. The system of claim 13, wherein the first peak emission wavelength is in a range from 440 to 455 nm and the second peak emission wavelength is in a range from 510 to 525 nm.

15. The system of claim 14, wherein the first phosphor comprises at least one of:

a) an $AMgAlO:Eu^{2+}$ phosphor where A comprises at least one of Ba, Ca or Sr;

b) a $DPOCl:Eu^{2+}$ phosphor where D comprises at least one of Sr, Ba, Ca or Mg;

c) an $EO*AlO:Eu^{2+}$ phosphor, where E comprises at least one of Ba, Sr or Ca;

d) an EAlO:Eu^{2+} phosphor, where E comprises at least one of Ba, Sr or Ca; or

e) a GAlO:Eu^{2+} phosphor, where G comprises at least one of K, Li, Na or Rb.

16. The system of claim 15, wherein the second phosphor comprises at least one of:

f) an AMgAlO:Eu^{2+},Mn^{2+} phosphor where A comprises at least one of Ba, Ca or Sr;

g) an EO*AlO:Eu^{2+},Mn^{2+} phosphor, where E comprises at least one of Ba, Sr or Ca;

h) an EAlO:Eu^{2+},Mn^{2+} phosphor, where E comprises at least one of Ba, Sr or Ca; or

i) a GAlO:Eu^{2+},Mn^{2+} phosphor, where G comprises at least one of K, Li, Na or Rb.

17. The system of claim 15, wherein:

the AMgAlO:Eu^{2+} phosphor comprises $AMg_2Al_{16}O_{27}:Eu^{2+}$, where A comprises at least 90% Ba;

the DPOCl:Eu^{2+} phosphor comprises $(Sr,Ba,Ca,Mg)_5(PO_4)_3Cl:Eu^{2+}$;

the AMgAlO:Eu^{2+},Mn^{2+} phosphor comprises $AMg_2Al_{16}O_{27}:Eu^{2+},Mn^{2+}$, where A comprises at least 90% Ba;

the EO*AlO:Eu^{2+} phosphor comprises $xBaO*6Al_2O_3:Eu^{2+}$;

the EAlO:Eu^{2+} phosphor comprises $(Ba_{1-x}Eu_x)Al_{12}O_{19}$; and

the GAlO:Eu^{2+} phosphor comprises $(K_{1-x}Eu_x)Al_{11}O_{17}$;

the EO*AlO:Eu^{2+},Mn^{2+} phosphor comprises $xBaO*6Al_2O_3:Eu^{2+},Mn^{2+}$;

the EAlO:Eu^{2+},Mn^{2+} phosphor comprises $(Ba_{1-x}Eu_x)Al_{12-y}Mn_yO_{19-0.5y}$; and

the GAlO:Eu^{2+},Mn^{2+} phosphor comprises $(K_{1-x}Eu_x)Al_{11-y}Mn_yO_{17-0.5y}$.

18. The system of claim 17, wherein:

the $AMg_2Al_{16}O_{27}:Eu^{2+}$ phosphor comprises $(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$, where $0 < x \leq 0.2$;

the $(Sr,Ba,Ca,Mg)_5(PO_4)_3Cl:Eu^{2+}$; phosphor comprises $(Sr_{1-y-z}Ba_yCa_z)_{5-x}Eu_x(PO_4)_3Cl$, where $0.01 \leq x \leq 0.2$, $0 \leq y \leq 0.1$ and $0 \leq z \leq 0.1$.

the $AMg_2Al_{16}O_{27}:Eu^{2+}$ phosphor comprises $(Ba_{1-x}Eu_x)Mg_{2-y}Mn_yAl_{16}O_{27}$, where $0 < x \leq 0.2$ and $0 < y \leq 0.5$;

the $xBaO \cdot 6Al_2O_3:Eu^{2+}$ phosphor comprises $Ba_{0.77}Eu_{0.03}Mn_{0.20}Al_{10.9}O_{17.2}$.

the $(Ba_{1-x}Eu_x)Al_{12-y}Mn_yO_{19-0.5y}$ phosphor comprises $(Ba_{0.86}Eu_{0.14})Al_{11.56}Mn_{0.44}O_{18.80}$; and

the $(K_{1-x}Eu_x)Al_{11-y}Mn_yO_{17.07-0.5y}$ phosphor comprises $(K_{0.86}Eu_{0.14})Al_{10.80}Mn_{0.20}O_{16.97}$.

19. The system of claim 18, wherein:

the first phosphor comprises $(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$, where $0 < x \leq 0.2$; and

the second phosphor comprises $(Ba_{1-x}Eu_x)Mg_{2-y}Mn_yAl_{16}O_{27}$, where $0 < x \leq 0.2$ and $0 < y \leq 0.5$.

20. The system of claim 19, wherein the at least one luminescent material (21) comprises the first phosphor and the second phosphor in a weight ratio of about 30:70 to about 8:92.

21. The system of claim 20, wherein the weight ratio of the first phosphor to the second phosphor is about 18:82.

22. The system of claim 21, wherein:

the first phosphor and the second phosphor are interspersed; or

the first phosphor and the second phosphor comprise discrete overlying layers.

23. The system of claim 13, wherein at least one of the first phosphor or the second phosphor comprises a blend of at least two phosphors.

24. The system of claim 1, further comprising:

a shell (17) containing the light emitting diode (11):

an encapsulating material (19) between the shell (17) and the light emitting diode (11); wherein at least one luminescent material comprises at least one phosphor, and

a) the phosphor is coated over a surface of the light emitting diode (11);

b) the phosphor is interspersed in the encapsulating material (19); or

c) the phosphor is coated onto the shell (17).

25. The system of claim 24, further comprising:

a traffic signal housing (43) containing the blue-green illumination system (51); and

a traffic light lens (45) in front of the blue-green illumination system (51).

26. The system of claim 1, wherein radiation emitted from a Eu^{2+} activator results in a first peak emission wavelength and radiation emitted from a Mn^{2+} activator results in a second peak emission wavelength.

27. A traffic signal (41) comprising:

a housing (43);

at least one lens (45);

a radiation source (1) having a peak emission wavelength of 420 nm and below; and

at least one luminescent material (3) having at least two peak emission wavelengths, wherein the emission CIE color coordinates of the at least two peak emission wavelengths are located within an area of a quadrilateral on a CIE chromaticity diagram, whose corners have the following CIE color coordinates:

a) x=0.000 and y=0.506;
b) x=0.224 and y=0.389;
c) x=0.280 and y=0.450; and
d) x=0.000 and y=0.730.

28. The traffic signal of claim 27, wherein the radiation source (1) comprises a light emitting diode (11).

29. The traffic signal of claim 28, wherein the emission CIE color coordinates of the at least two peak emission wavelengths are x=0.1 ± 0.05 and y=0.52 ± 0.05.

30. The traffic signal of claim 29, wherein the at least one luminescent material (1) comprises a blend of a $(Ba_{1-x}Eu_x)Mg_2Al_{16}O_{27}$ phosphor, where $0 < x \leq 0.2$, and a $(Ba_{1-x}Eu_x)Mg_{2-y}Mn_yAl_{16}O_{27}$ phosphor, where $0 < x \leq 0.2$ and $0 < y \leq 0.5$ in a weight ratio of about 30:70 to about 8:92.

31. The traffic signal of claim 30, wherein the weight ratio is about 18:82.

32. A method of making a blue-green light illumination system, comprising:
blending a first phosphor powder having a first peak emission wavelength and a second phosphor powder having a second peak emission wavelength to form a phosphor powder mixture having emission CIE color coordinates located within an area of a pentagon on a CIE chromaticity diagram, whose corners have the following CIE color coordinates:
e) x=0.0137 and y=0.4831;
b) x=0.2240 and y=0.3890;
c) x=0.2800 and y=0.4500;
g) x=0.2879 and y=0.5196; and
h) x=0.0108 and y=0.7220; and

placing the phosphor powder mixture (3, 21) into the illumination system adjacent a radiation source (1).

33. The method of claim 32, wherein the radiation source (1) comprises a light emitting diode (11).

34. The method of claim 33, wherein:

the light emitting diode (11) peak emission wavelength is between 370 and 405 nm; and

the phosphor powder mixture (21) emission CIE color coordinates are x=0.1 ± 0.05 and y=0.52 ± 0.05.

35. The method of claim 34, wherein the step of blending comprises blending a first phosphor powder selected from at least one of:

a) a $AMgAlO:Eu^{2+}$ phosphor where A comprises at least one of Ba, Ca or Sr; or

b) a $DPOCl:Eu^{2+}$ phosphor where D comprises at least one of Sr, Ba, Ca or Mg; and

a second phosphor powder selected from at least one of:

c) a $AMgAlO:Eu^{2+},Mn^{2+}$ phosphor where A comprises at least one of Ba, Ca or Sr;

d) an $EaO*AlO:Eu^{2+},Mn^{2+}$ phosphor, where E comprises at least one of Ba, Sr or Ca;

e) an $EAlO:Eu^{2+},Mn^{2+}$ phosphor, where E comprises at least one of Ba, Sr or Ca; or

f) a $GAlO:Eu^{2+},Mn^{2+}$ phosphor, where G comprises at least one of K, Li, Na or Rb.

36. The method of claim 35, wherein the step of blending the first phosphor powder and the second phosphor powder comprises blending (Ba$_{1-}$

$_x Eu_x)Mg_2Al_{16}O_{27}$, where $0 < x \leq 0.2$, and $(Ba_{1-x}Eu_x)Mg_{2-y}Mn_yAl_{16}O_{27}$, where $0 < x \leq 0.2$ and $0 < y \leq 0.5$ in a weight ratio of about 30:70 to about 8:92.

37. The method of claim 36, wherein the weight ratio is about 18:82.

38. The method of claim 33, further comprising:
placing the light emitting diode (11) into a shell (17); and
filling the shell (17) with an encapsulating material (19).

39. The method of claim 38, further comprising:
a) coating a suspension of the phosphor powder mixture and a solvent over a surface of the light emitting diode (11) and drying the suspension;
b) interspersing the phosphor powder mixture (21) in the encapsulating material (19); or
c) coating a suspension of phosphor powder mixture and a solvent onto the shell (17) and drying the suspension.

40. The method of claim 32, wherein the emission CIE color coordinates of the phosphor powder mixture (21) are located within an area of a quadrilateral on a CIE chromaticity diagram, whose corners have the following CIE color coordinates:
a) $x=0.000$ and $y=0.506$;
b) $x=0.224$ and $y=0.389$;
c) $x=0.280$ and $y=0.450$; and
d) $x=0.000$ and $y=0.730$.

41. The method of claim 40, further comprising placing the illumination system (51) into a traffic signal housing (43).

42. The method claim 32, wherein the emission CIE color coordinates of the phosphor powder mixture are located within an area of a quadrilateral on a CIE chromaticity diagram, whose corners have the following CIE color coordinates:

e) x=0.0137 and y=0.4831;
f) x=0.2094 and y=0.3953;
g) x=0.2879 and y=0.5196; and
h) x=0.0108 and y=0.7220.

43. The method of claim 42, further comprising placing the illumination system into an automotive display.

FIG. 1

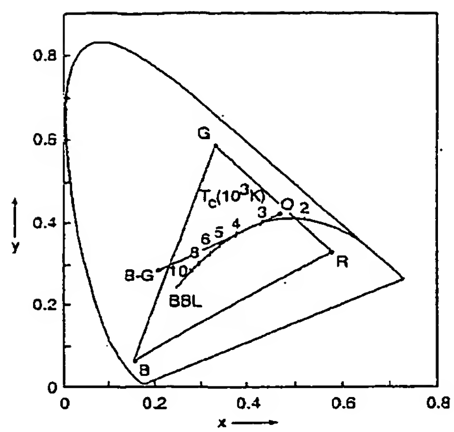


FIG. 2

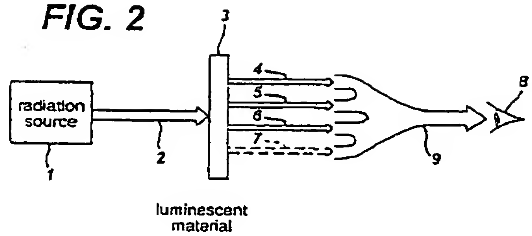


FIG. 3

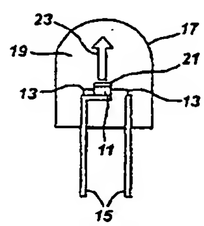


FIG. 4

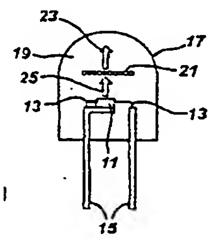


FIG. 5

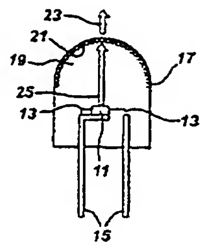


FIG. 6

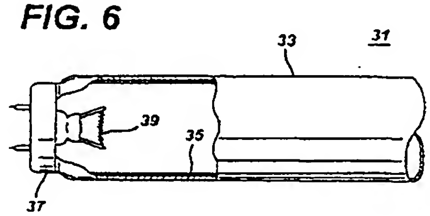
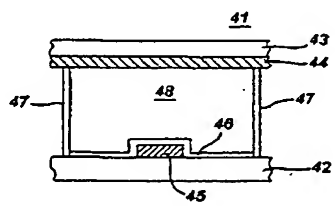


FIG. 7



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